

PECREST

Plastics chemical recovery for production of chemical intermediates at a Swedish chemical complex

An EIT climate-KIC pathfinder project

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Preface

This report presents the activities of the PECREST project, a collaboration between Chalmers University of Technology, Borealis AB, and Stena Recycling International AB. The project was financed by EIT Climate-KIC under the thematic area “industrial symbiosis”.

The project started in august 2015 and ended in February 2016.

Matteo Morandin was the project leader and worked mainly with the modelling and simulation of the methanol and ethanol synthesis and of the pyrolysis section, as well as with the estimation of the process integration opportunities and GHG emission reduction potentials of the proposed processes. Stefan Heyne has worked mainly with modelling and simulation of the biomass and plastic gasification section, and helped with definition of process layouts.

Marianne Gyllenhammar and Henrik Jilvero at Stena Metall and Lars Pettersson at Borealis AB were the main representatives of the industrial partners who were actively involved in discussions as well as in the final editing of this report.

Simon Harvey at the div. of Industrial Energy Systems and Technologies, Chalmers University of Technology, was also actively involved in discussions.

Maria Arvidsson at the div. of Industrial Energy Systems and Technologies, Chalmers University of Technology, is gratefully acknowledged for her help on process modelling and on estimation of GHG emissions reduction potentials.

Matteo Morandin

Gothenburg, 14 March 2016

Summary

The present report discusses process concepts for chemical recycling of waste streams for production of chemical intermediates at a Swedish chemical complex site.

The total Swedish waste stream of plastics, automotive shredder residues (ASR) and electronic waste (WEEE) currently sent to energy recovery were considered and metal recovery was also considered for the relevant streams. Forest residues were also used as an input following a vision of feedstock flexibility and carbon-neutral production of chemicals.

The layout of the envisioned waste-to-chemical plant includes a process for production of ethylene via gasification of plastics and forest residues and a process for production of syngas for OXO-synthesis applications via pyrolysis of ASR and WEEE.

Mass and energy balances were established by process flowsheet simulations and process integration opportunities were identified by applying an energy targeting methodology. Finally, the GHG emission reduction potentials of such processes were quantified by keeping the energy recovery alternative as reference of comparison.

Based on rather optimistic assumptions it was found that about 120 kt of ethylene per year and about 44 kt of syngas can be produced which are respectively about 15% and 26% of the site demand of ethylene and syngas to OXO synthesis.

Overall, the estimated contribution to global GHG emission reduction lies in a range between 800 and 1300 kt CO₂-eq per year depending on the different scenarios of marginal technologies for production of ethylene, electricity and heat. This is about the same order of magnitude of the current on-site GHG emissions at the Stenungsund chemical complex site. This result is based on the assumption that chemical recycling is alternative to energy recovery which in Sweden is done in CHP units connected to district heating networks. By diverting waste to chemical production, we assumed that biomass CHP units compensate for electricity and heat production and that this can even create a surplus of electricity in short term which in turns reduces the production of electricity in coal power plants. This results highlights that the climate consequences of the proposed recycling strategy are largely dependent, at least in Sweden, on the future development of the biomass prices and utilization.

The results also show that an important reduction of GHG emissions can be obtained by recovering the large amounts of excess heat available from the thermochemical processes for production of steam which can be exported to the various chemical plants by appropriately placing the proposed processes close to or in the middle of the chemical complex site. This steam is about 70% of the steam currently produced at the site in natural gas boilers. The reduction of natural gas consumptions in steam boiler contributes to about 20 to 30% of the total GHG emission reduction potential which highlights the suitability of the Stenungsund site for large-scale implementation of biorefineries and waste-to-chemical plants.

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Introduction

1.1 Project objectives

The aim of this study was to perform a screening of innovative concepts for production of chemical feedstock for the chemical complex site in Stenungsund (Sweden) starting from pyrolysis and gasification of recovered plastic, forest residues and, if feasible, other waste. A limited number of promising process layouts were selected and their mass, energy and GHG emission balances assessed.

Starting from previous studies focusing on biomass feedstock only, the objective was to expand the assessment of technological options for switching from the current fossil based production to a more carbon neutral production using a biomass/recycle based refinery plant to substitute a significant fraction of current petrochemical feedstock for production of chemical intermediates.

The intrinsic material and energy integration opportunities at the Stenungsund site are of primary importance to achieve high resource efficiency and were therefore taken in detailed consideration.

1.2 Report structure

This report is structured as follow.

In this introductory chapter, an overview of the Stenungsund chemical complex is given and the option of plastic thermochemical recycling for production of chemical intermediates at the Stenungsund chemical complex is introduced.

In the Chapter 2 the amount and characteristic of plastic waste in Sweden is presented and from that the input waste streams to the thermochemical recycling processes at the Stenungsund chemical complex site is derived.

In the Chapter 3, an overview of the technology for thermochemical recycling is given based on a literature survey.

The methodology adopted in this study is introduced in Chapter 4 which include an overview of the modelling assumptions for the various thermochemical processes, of the energy targeting method used for estimating the steam export from the waste-to-chemical processes to the existing chemical plants, and of the assumptions for estimating the global GHG emission reduction that can potentially be achieved by implementing the proposed processes.

The resulting mass and energy balances as well as the estimated GHG emission reduction potentials for the proposed processes are presented in Chapter 5.

Finally conclusive remarks are given in Chapter 6.

1.3 Sustainable production of chemicals and plastics

The largest Swedish chemical complex is located in Stenungsund on the West Coast of Sweden. As shown in Figure 1, the site consists of six main plants producing a variety of different chemical products and is owned by five different major international chemical companies.

Borealis is the main producer of olefins and polyethylene (HDPE, LDPE) starting from hydrocarbon steam cracking. Perstorp produces OXO-alcohols, specialty chemicals and also bio-diesel (RME). Inovyn produces caustic soda mainly for the pulp and paper industry, vinyl chloride monomer and PVC. Akzo Nobel produces amines and surfactants. AGA, member of the Linde group, produces industrial gases such as oxygen and nitrogen.

The chemical complex currently features high material integration between the different production sites, where ethylene is the main chemical intermediate for polymers, alcohols, ethylene oxide, ethylene glycol and the base for large variety of further value-chains.

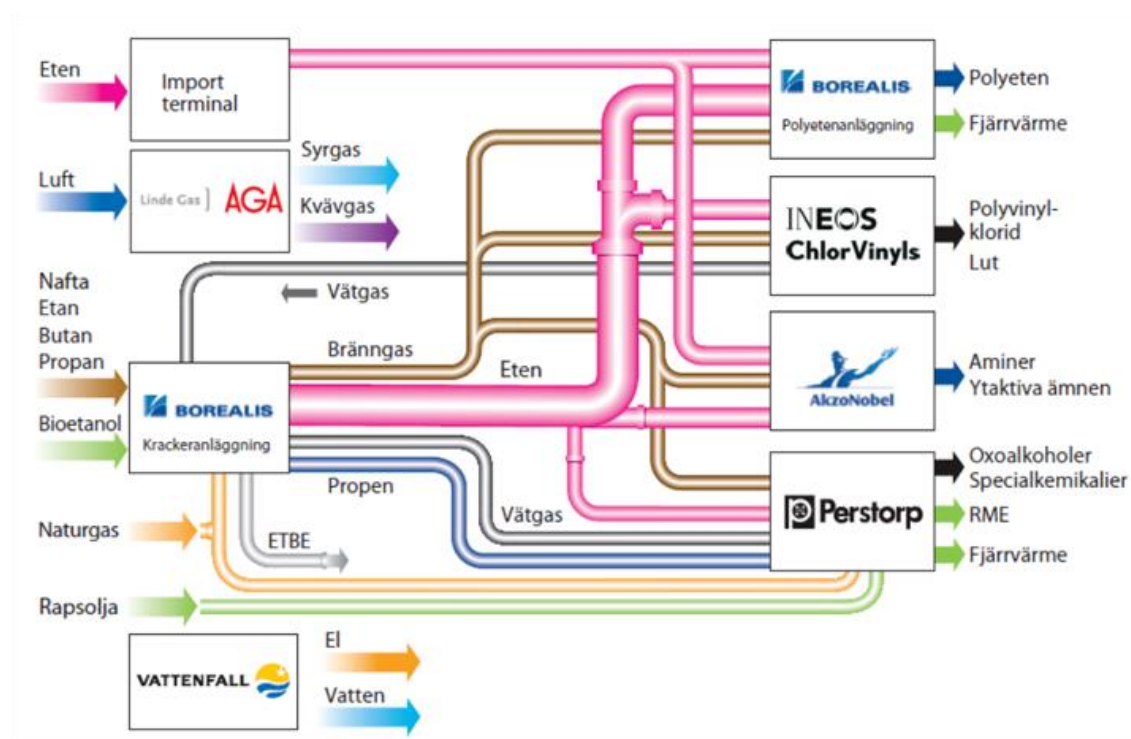


Figure 1: Processes, companies and main material flows of the Stenungsund chemical complex site (note: Since July 2015 INEOS ChloroVinyls has changed name into INOVYN, a joint venture between INEOS and Solvay)

The companies have recently adopted a common vision, Sustainable Chemistry 2030, to increase the complex's energy efficiency and to reduce its fossil feedstock dependence by switching to carbon-neutral productions of chemicals. The integration of biogenic feedstock has been primarily considered not only by importing green drop-in chemicals from the market but also by integration of fully developed biorefinery concepts that process biomass into different chemical intermediates or products (Joelsson et al., 2015). Recently, the option of processing waste streams in combination with biomass has also been advanced to increase feedstock flexibility, a key feature for producers of chemicals especially in countries lacking direct access to cheap fossil feedstock.

To foster a transition to more sustainable production systems, the organization “West Swedish Chemical and Material Cluster” has also been created to promote collaborations between companies also outside the boundaries of the Stenungsund chemical complex. This includes companies such as the Preem refinery, the energy service company of the city of Gothenburg Göteborg Energi which owns the largest demonstration plant for bio-SNG production, and Stena Recycling International a world leader in waste recycling. Chalmers University of Technology is also part of this cluster and contributes mainly with research activities.

Industrial clusters and, in particular, large petrochemical sites, have several opportunities for energy efficiency solutions that can lead to significant reduction of GHG emissions. A recent PhD project by Roman Hackl has shown feasible heat recovery options and exchange of heat between the Stenungsund companies to reduce the natural gas consumption for steam production (Hackl, 2014). Recovery of excess heat from the Stenungsund chemical plants is also the topic of an ongoing industrial licentiate project (Lina Eriksson, SP Sweden, Chalmers IEST since 2013) where competition between internal use of excess heat and export to the district heating network is investigated. The different size and characteristics of the chemical plants are reflected by different shares of heat being released or consumed (Eriksson et al., 2015). Due to the different plant ownerships, collaborations between the different companies is a crucial aspect and new business models together with transparent price mechanism for the exchanged energy commodities are required.

Beside technological advancements or increased heat collaborations between chemical plants, the most common option considered to mitigate the GHG emissions associated with production of chemicals is the use of renewable feedstock such as biomass as a source of carbon and hydrogen for subsequent synthesis of chemical intermediates.

In Gothenburg, the GoBiGas project has built a commercial-scale demonstration plant for the production of 20 MW of substitute natural gas (SNG) from gasified wood biomass. SNG can be used as a car fuel similarly to biogas from waste. However, natural gas is also a common feedstock for production of chemicals, in particular for production of syngas which is widely used for hydroformylation of olefins into aldehydes as currently performed at the Stenungsund cluster by Perstorp. In a recent project carried out by Maria Arvidsson, the application of biomass gasification for production of SNG and its integration with the Stenungsund chemical site has been investigated. This option has been compared with directly producing syngas as a feedstock for oxo-synthesis applications (Arvidsson et al., 2015b). The advantages of direct syngas production compared to reforming bio-SNG have been quantified in terms of resource efficiency, process economics and global GHG emissions (carbon footprint). It was found that bio-syngas production for OXO-synthesis has more favourable process economics than most other biomass gasification based biorefineries.

In the recent Skogskemi project the production of methanol via gasification of biomass has been investigated (Joelsson et al., 2015, Morandin and Harvey, 2014). In addition to its use as motor fuel, methanol (or DME) represents an interesting starting point for subsequent conversion into high value chemicals such as olefins via the methanol-to-olefins (MTO) technology which can potentially replace or partially substitute the conventional olefin production via naphtha crackers, currently performed in Stenungsund by Borealis. A life cycle and techno-economic analysis of production of around 20% of the current olefin production at Borealis via MTO has been performed. Results show that the adoption of MTO technology can largely affect the steam balance at the cracker. However, if methanol is produced via biomass gasification located within the Stenungsund chemical complex site, the excess heat from biomass gasification is able to cover a large part of the high pressure

steam demand of the cracker plant thus potentially replacing the fuel currently burned in steam boilers (Arvidsson et al., 2015a).

All these studies have confirmed and quantified the environmental benefits of biomass utilization as feedstock for production of chemicals with technologies that are technically feasible although yet not fully commercialized. Except possibly for the bio-syngas case, the major barriers are related to unfavourable process economics with present policy instruments, which are more favourable for utilization of biomass in the energy sector. In addition, in Sweden, biomass is an important feedstock for the pulp and paper industry. The limited availability of biomass raises important environmental concerns and uncertainty in future price scenarios also in a country like Sweden where lignocellulosic biomass is abundant. More stringent GHG emission limits may be imposed to the energy and transportation sectors in a near future which is expected to increase the demand for lignocellulosic biomass and therefore to further limit the access of the chemical industry to cheap renewable source of carbon.

1.4 Plastic chemical recycling

Waste can be used as a source of organic carbon and may represent an alternative to biomass when looking at more sustainable production of chemical and plastics. In this project we have focused on the valorisation of plastic waste streams by means of plastic thermochemical recycling.

Plastic recycling can be categorized in three main types: (1) material recycling, (2) chemical recycling, (3) energy recovery.

Material recycling consists in recycling the plastic by mechanical means for production of new products thus directly replacing virgin plastics. Although in reality the recycled polymers cannot achieve the same purity of virgin plastic and the degree of material recycling is therefore limited, this recycling strategy allows the highest reduction of global GHG emissions for production of new products and should be therefore preferred. The target for Sweden in 2020 is to have at least 30% material recycling which is expected to increase to 50% sometime after 2020 according to EU directives (European Union, 2008).

At the opposite side of the recycling cascade is energy recovery which consists in combustion of plastics in so-called waste-to-energy plants for production of electricity and heat. Compared to landfilling or incineration without energy recovery, energy recovery represent an economic opportunity for getting rid of waste while reducing the consumption of other valuable resources for production of electricity or heat. It is currently the most common waste handling strategy in Europe, especially in the northern countries where heat recovery represent a bigger share of income due to past investment in district heating networks. Since all the carbon in the material is ultimately released in CO₂ after combustion, and since there is no direct reduction of virgin plastic production, the impact on global GHG emissions of energy recovery is significantly determined by the alternative energy conversion technologies for production of electricity and heat in the region. This strategy may be in the long-term reduced in presence of progressively larger share of material recycling and with increasing availability of renewable electricity and heat.

Chemical recycling represents another way to avoid complete combustion of plastic and to recover at least part of the polymer or of its building blocks into production of new products. This can consist in chemical decomposition of plastic waste and recycle of valuable polymers by separation or medium and high temperature thermochemical decomposition of plastic waste, for instance by pyrolysis or gasification. The latter allows to recover part of the polymer building blocks into petrochemical feedstock. The product is usually a mixture of a solid fraction (mainly char), a liquid and a gaseous phase. Depending on the substrate (e.g. polymer types) and on process temperature and residence time, the gaseous

and liquid phases can be of different natures, but applications such as motor fuel or as chemical intermediates have been considered in the past.

Although no significant differences in technology may appear between different applications, the difference between recovering plastic waste into motor fuels or chemical intermediates may be dramatic from a life-cycle perspective. Only recovering the chemical elements of plastics into new plastics can be regarded as close-loop recycling. Plastic derived motor-fuels are indeed another way to fully release the plastic carbon in form of CO₂ to the atmosphere, and their impact on global GHG emission is therefore largely dependent on the future of the transportation sector. Thermochemical recycling should be regarded as an alternative to energy recovery if a cycle of carbon is achieved, for instance if carbon from plastic waste is used to produce similar or the same polymers.

A detailed life-cycle assessment of plastic waste treatment technologies for the Greater London area (Al-Salem et al., 2014) shows that the combination of advanced plastic material recycling and waste-to-energy plants is the best option from a global warming impact. However it was found that when material recycling products cannot fully substitute the virgin plastic, thermochemical recycling is a better option.

The issue about degree of substitution is also highlighted in (Lazarevic et al., 2010) where a comparison is made between different LCA studies on plastic recycling. When only looking at global warming potential, it is clear that material recycling results always better compared to other strategies. Feedstock recycling appears however always better than energy recovery although results can be very different between different feedstock recycling processes.

A study by University of Naples of 2005 (Perugini et al., 2005), discusses in detail the LCA of different plastic waste recycling strategy. Particularly interesting is the comparison between mechanical recycling and two feedstock recycling options for polyolefins fractions: low temperature pyrolysis (BP polymer cracking) and hydrocracking (Veba Combi-Cracking). The global warming impact of the feedstock recycling processes appears quite similar and the estimated total GHG emission saving potential compared to combustion with energy recovery is substantial (about 5 kg CO₂-eq per kg recycled plastics).

A petrochemical complex site is a suitable site for integration of plastic chemical recycle since multiple options are already in place for using different types of hydrocarbons and syngas for production of chemicals.

In fact it appears that studies on feedstock recycling from plastic waste in the Swedish context have so far not been published, at least at a conceptual level as done in the PECREST project. In this project we mainly investigated the production of syngas from which methanol, ethanol and finally ethylene are produced. Additionally, compared to other studies in the literature, the proposed processes are not considered on their own but are located in the proximity of a chemical complex site thus opening significant material and heat integration opportunities. In particular, this allows valorising the large amount of excess heat from the thermochemical processes used for waste recycling by exporting steam to the existing chemical plants and in this way introducing significant natural gas savings. The proposed processes can be therefore considered as of a combined feedstock and energy recovery type.

1.5 Opportunities for combined feedstock and metal recycling

Automotive shredder residues (ASR) and electronic waste (WEEE) are two waste streams which are rich in plastics but also in metals.

The majority of the various parts of end-of-life vehicles are recycled but about 25% of the vehicle is sent to shredding. The residue, ASR, is a mix of metal, plastics and other organic and inorganic materials. The amount of ASR in western countries is steadily increasing and therefore effective solution for ASR disposal are of high interest. Landfilling and combustion, either in waste-to-energy plants or in cement kiln, are the two most common strategies. However, ASR pyrolysis and gasification have been demonstrated and are attractive solutions although the environmental advantage over energy recovery is largely depending on the process characteristics and on the type of application (Vermeulen et al., 2011). This is somewhat confirmed by a study by University of Bologna of 2010 (Ciacci et al., 2010), in which the life-cycle assessment of different ASR treatment processes is discussed. In this study it appears that feedstock recycling can introduce similar environmental benefits as advanced material recycling with integrated incineration.

It should be observed however that an opportunity offered by low temperature pyrolysis, is the fact that metals, after pyrolysis, remain in the solid fraction. Since their concentration is much higher than in the original material, metals can be recovered prior sending the char and the other inert material to combustion. This may allow higher degree of metal recovery than from combustion ashes from incinerators (Bunge, 2015).

Material recycling of electronic waste (WEEE) is much more difficult than for the ASR case and therefore landfilling and combustion of selected fractions is the most common way to take care of end-of-life electronics. Thermochemical recycling is an option but still needs to be proved as commercially viable solutions (Tukker, 2012).

Feedstock recycling from WEEE treatment has so far not been studied in detail from a system aspect point of view, life-cycle assessment being mostly conducted for advance material recycling concepts (Wager and Hischer, 2015).

Besides the presence of metals, ASR and WEEE share some other common features:

- They contain a variety of rather complex plastic resins for which material recycling is not commercially available.
- ASR contain a significant quota of PVC and WEEE contain plastics with flame-retardants which leads to non-negligible amounts of Chlorine or Bromine in the products of thermochemical decomposition.
- ASR and WEEE compositions are continually changing due to changing characteristics of consumer products (cars, electronics, etc.) and it is particularly difficult to tailor a treatment process for a specific product.

2 Plastic waste streams characterization

2.1 Relevant polymer types

The most common polymer types according to Plastic Europe (Plastics Europe, 2012) are in order of demand:

- Polypropylene (PP).
- Low density polyethylene (LDPE).
- High density polyethylene (HDPE).
- Polyvinyl chloride (PVC).
- Polystyrene (PS).
- Polyethylene terephthalate (PET).
- Polyurethane (PUR).

Other relevant polymers that are used in different consumer products are:

- Acrylonitrile butadiene styrene (ABS).
- Polycarbonates (PC), hereafter considered assumed as Bisphenol A polycarbonate.
- Polymethyl methacrylate (PMMA).
- Polyamides of different kinds (PA), hereafter assumed as Nylon 66.

To estimate the product yields of thermochemical decomposition of plastics, it is necessary to know the amount of chemical elements of the different polymers. The proximate and ultimate analyses of the relevant polymer types are shown in Table 1 and in Table 2. From the ultimate analysis is possible to calculate the higher heating value (HHV) of a given material on dry basis. The equation provided by Channiwala and Parikh was used for this purpose (Channiwala and Parikh, 2002). Note that the moisture content of plastic is negligible so the HHV on dry basis is substantially similar to the actual HHV.

Note also that for PC, PMMA and PA it was not possible to retrieve any reliable data about proximate or ultimate analysis. For these resins the ultimate analysis was simply calculated based on reference chemical formula.

In Table 1 and in Table 2, the proximate and ultimate analyses of ASR, WEEE and forest residues are also reported since these are other type of materials (waste streams) that are also considered among the input to the thermochemical recycling processes.

The composition of ASR and WEEE is here assumed based on the data provided by the project partner Stena Metall. These are data for the fractions of ASR and WEEE that are today sent to energy recovery. The acronym SLF which stands for “shredder light fraction” is also used by Stena Metall to address the ASR fraction rich in plastics and is also used in sometimes in this report.

Table 1: Proximate analysis of relevant plastic resins and materials. (* assumed)

Plastic resin	Fixed Carbon (wt-% dry)	Volatile Matter (wt-% dry)	Ash (wt-% dry)	Moisture (wt-% a.r.)	Reference
PP	0	99.9	<0.05	0.13	(Zevenhoven et al., 1997)
LDPE	0	99.9	<0.05	0.10	"
HDPE	0	99.9	<0.05	0.16	"
PVC	7.5	92.3	<0.05	0.18	"
PS	0	97.0	2.89	0.11	"
PET	12.0	88.0	0.04	0	(Senneca et al., 2002)
PUR	2.1	97.9	0	0	(Kim et al., 2006)
ABS	0	100	0	0	(Encinar and González, 2008)
PC	na	100 *	na	na	na
PMMA	na	100 *	na	na	na
PA	na	100 *	na	na	na
ASR-SLF	na	48 *	40	12	Stena Metall
WEEE	na	80 *	12	8	Stena Metall
Forest residues	20	77.86	2.14	40	(Wilk and Hofbauer, 2013a).

Table 2: Ultimate analysis of relevant plastic resins and materials (*measured, not by difference).

Plastic resin	C (wt-% dry)	H (wt-% dry)	N (wt-% dry)	Cl (wt-% dry)	S (wt-% dry)	O (wt-% dry)	Ash (wt-% dry)	Calculated higher heating value (MJ/kg-dry)
PP	85.5	14.3				0.19*	<0.05	46.68
LDPE	85.7	14.3				0.16*	<0.05	46.75
HDPE	85.6	14.2				0.30*	<0.05	46.58
PVC	40.1	5.1		53.8		0.65*	<0.05	19.94
PS	88.9	8.3				0.16*	2.89	40.74
PET	62.8	4.3	0.07			32.79	0.04	23.60
PUR	59.8	8.4	6.0			25.80	0	28.02
ABS	82.06	8.89	5.09	0.11	0.09	3.76	0	38.67
PC	78.95	5.51				18.9	na	30.93
PMMA	60.00	8.00				32.00	na	27.06
PA	63.72	9.73	12.39			14.16	na	32.06
ASR-SLF	35.3	4.5	0.9	1.2	0.3	17.8	40	14.96 (13.16 as received)
WEEE	70.6	6.5	1.7	0.7		13.0	8	33.35 (29.35 as received)
Forest residues	48.93	5.87				43.06	2.14	19.5 (11.7 as received)

2.2 Overview of plastic recycling in Sweden

According to the report “Kartläggning av plastavfallsströmmar i Sverige” (Fråne et al., 2012), the amount of plastic in the Swedish market in year 2010 was about 900 kt. Despite the advancement in traceability of waste streams in the last decades, the total amount of plastic waste stream quantified for year 2010 was about 560 kt.

The difference (340 kt per year) between the total amount of plastic in the market and the estimated plastic waste stream may be explained partially by the fact that the above estimates are based on data from those recycling companies that operate in districts where more advanced recycling systems are used compared to the remaining parts of the countries. Furthermore, it has been advanced that although the demand of plastics has increased dramatically in the recent decades plastic is also stored in society and even if the plastic market would remain constant the amount of plastic waste may grow larger for a while (Fråne et al., 2012).

As shown in Figure 2, Fråne et al. quantified that about 26 % of the total estimated plastic waste stream for year 2010 went to material recycling (91 kt in Sweden, 53 kt export), about 58% went to energy recovery (321 kt), about 14% was used as fuel in cement industry (79 kt), and about 2% was landfilled (7 kt in Sweden, 5 kt export) (Fråne et al., 2012).

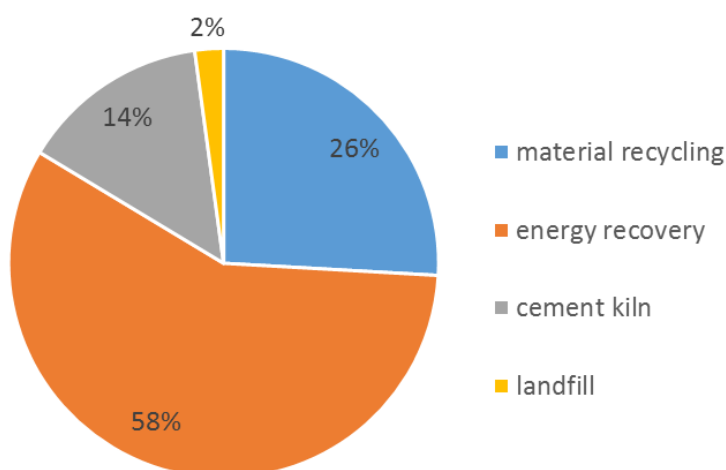


Figure 2: Overview of plastic waste treatment in Sweden for the year 2010 as estimated in (Fråne et al., 2012).

In addition to the 560 kt of plastic waste, about 91 kt of plastic waste of unknown characteristics and end-use was exported, and an extra 300 kt of plastic waste was imported mainly from Norway and used for energy purposes in Sweden. Assuming that the estimates in (Fråne et al., 2012) are correct, it can be concluded that the energy recovery (i.e. heat and power production) is today significantly oversized compared to available plastic waste stream from Swedish sources.

The Swedish target for plastic waste sent to material recycling is since 2012 of 30% but this should increase to 50% after 2020 according to EU directives (European Union, 2008).

One reason for the fact that material recycling does not seem to occur as expected is the fact that large amount of plastic from the domestic sector still ends up in unsorted residual waste.

From a 2009 report by University of Luleå (Dahlén and Vukicevic, 2009) it appears that in Sweden about 90% of plastic packaging in the residential sector still ends up in residual waste (i.e. energy recovery). However, in virtuous cities, only about 40 to 50 % of plastic packaging ends up in the residual waste. This indicates that the total flow of plastic waste stream sent to energy recovery may be largely reduced in the future if state-of-the-art sorting and recycling strategies are introduced. The same report, however, highlights that the contaminating fraction of wrongly sorted material that ends up in the sorted plastic is also increasing, thereby limiting the material recycling rate that can be achieved.

2.3 Characterisation of plastic waste streams that are potential feedstock for thermochemical recycling

In this study, the amount of plastic waste streams that can potentially be used as feedstock for thermochemical recycling was assumed equal to the amount generated in Sweden that today goes to energy recycling, to incineration (including the fraction used as fuel in cement industry), and to landfilling. We decided however to exclude the amount of plastic waste today imported from other countries or the amount of plastic that is exported for which data about composition or end-use are not available.

Data about the amount and characteristics of plastic waste streams in Sweden are sparse and seldom reported in a uniform way for the different regions.

As a starting point in this work, the report “Kartläggning av plastavfallsströmmar i Sverige” was used (Fråne et al., 2012).

The most recent data available are for year 2010 and are shown here in Table 3. As reported in (Fråne et al., 2012) such flows were calculated based on data from other sources and scaled up to the total Swedish population. These should be therefore considered as indicative data, and the actual flows may differ considerably. For instance the plastic waste stream in residual waste from the residential sector is largely dependent on the local recycling logistics which differ between cities or even districts.

Table 3. Flows of plastic waste in Sweden 2010 that go to energy recycling (incl. as fuel for cement industry) or landfilling in Sweden. Adapted from Table S1 in (Fråne et al., 2012).

SECTOR	End of life	FLOW (t/y)
Residential		
sorted plastic packaging	(Material recycling)	
plastic packaging in the residual waste	Energy recovery	151 000
other plastic in the residual waste	Energy recovery	42 000
plastic packaging in the sorted food waste	Energy recovery	1 000
sorted deposit bottles	(Material recycling)	
bulky waste	(Mat.recycl.)/En.rec.	36 000
<i>total residential</i>		<i>230 000</i>
Construction and demolition		
sorted plastic	(Material recycling)	
combustible and mixed waste	Energy recovery	43 000
<i>total construction and demolition</i>		<i>43 000</i>
End-of-life Electronics		
sorted electronics from residential	(Mat.recycl.)/Energy	9 500
sorted electronics from business	(Mat.recycl.)/Energy	3 000
electronics in residual waste	Energy	1 000
<i>total electronics</i>		<i>13 500</i>
End-of-life vehicles		
collected vehicles / demolition	Energy/Landfilling	12 000 / 6 000
<i>total vehicles</i>		<i>18 000</i>
manufacturing and services		
sorted plastic waste	(Mat.recycl.)/Energy/Cement	9000 / 79 000
<i>total manufacturing and services</i>		<i>88 000</i>
medical applications		
hazardous waste	Energy	13 000
<i>total medical applications</i>		<i>13 000</i>
agriculture		
plastic ensilage	Energy	2 000
<i>total agriculture</i>		<i>2 000</i>
<i>total Sweden</i>		<i>407 500</i>

2.3.1 Composition and amounts by sector

Data about composition of the various flows are also very difficult to obtain since the somewhat different recycling logistics introduce a large bias on what type of plastic ends up in the various flows, and since general purpose statistics usually do not have such level of detail.

2.3.1.1 Residential sector

It was possible to acquire some data about the composition of household waste from the Kretslopp & Vatten department of the city of Göteborg (Kretslopp & Vatten, 2015). Household waste may differ substantially depending on whether the food waste is separately sorted; the household waste including food waste is hereafter referred to as “unsorted waste”, whereas the waste without food waste is hereafter referred to as “residual waste”. In addition, there are differences between different house types and lifestyles that reflect on the amount of waste and its composition.

The composition of residual or unsorted waste according to the analyses done in nine different districts in the city of Göteborg is shown in Figure 3. The average percentage of plastic waste is shown in Table 4.

We followed a shortcut methodology proposed in (Fråne et al., 2012) to estimate the amount of plastics in household waste based on the data from (Kretslopp & Vatten, 2015) in order to see if a similar results are obtained.

The amount of household waste in Sweden in year 2012 was about 2 297 000 tonnes. About 60% of the Swedish population lives in cities where food waste is sorted (i.e. 40% lives in cities where food waste is not sorted). About 53.5% of the population in Sweden lives in apartments (i.e. 46.5% lives in villas).

If data about Göteborg are extrapolated to all Sweden according to the methodology proposed in (Fråne et al., 2012), the total amount of plastic stream in the household waste is:

$$2297000 \cdot [((0.19 \cdot 0.465) + (0.163 \cdot 0.535)) \cdot 0.6] + [(0.13 \cdot 0.465) + (0.160 \cdot 0.535)] \cdot 0.4 \cdot 0.56 = 211680 \text{ tonnes}$$

Note that a correction factor of 0.56 is also applied to the whole plastic waste stream to account for ashes and moisture in common household waste.

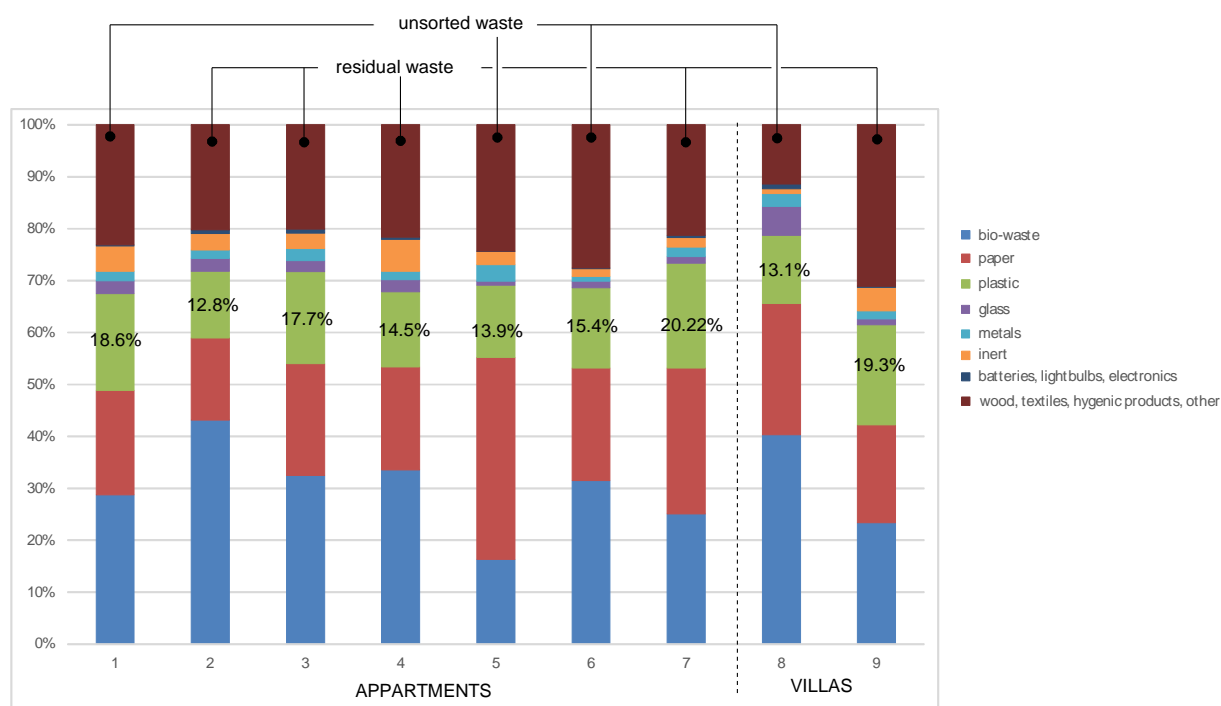


Figure 3: Composition of residual or unsorted waste from household in different districts in Göteborg (Kretslopp & Vatten, 2015).

Table 4: Percentage of plastic in residual or unsorted waste in apartments or villas according to the analyses provided in (Kretslopp & Vatten, 2015)

	Apartments	Villas
Residual waste	16.3%	19.3%
Unsorted waste	16.0%	13.1%

This number is in good agreement with the data reported in (Fråne et al., 2012) for the year 2010 of all plastic packaging and other plastic in the residual and unsorted waste (193 kt) calculated using data from other analyses, if also considered that the total amount of household waste increased by 7% from 2010 to 2012. For consistency with the assumptions made in this work for the other sectors, it was decided to retain the value reported in (Fråne et al., 2012) for year 2010 (193 kt). The data obtained from (Kretslopp & Vatten, 2015) show that this is probably a conservative estimate.

From the data from Kretslopp & Vatten, it is possible to estimate with more detail the amount of soft plastic and hard plastic packaging as well as other plastic types in the total flow of unsorted and residual waste which is a first step for more detailed composition analysis. These fractions are shown in Figure 4.

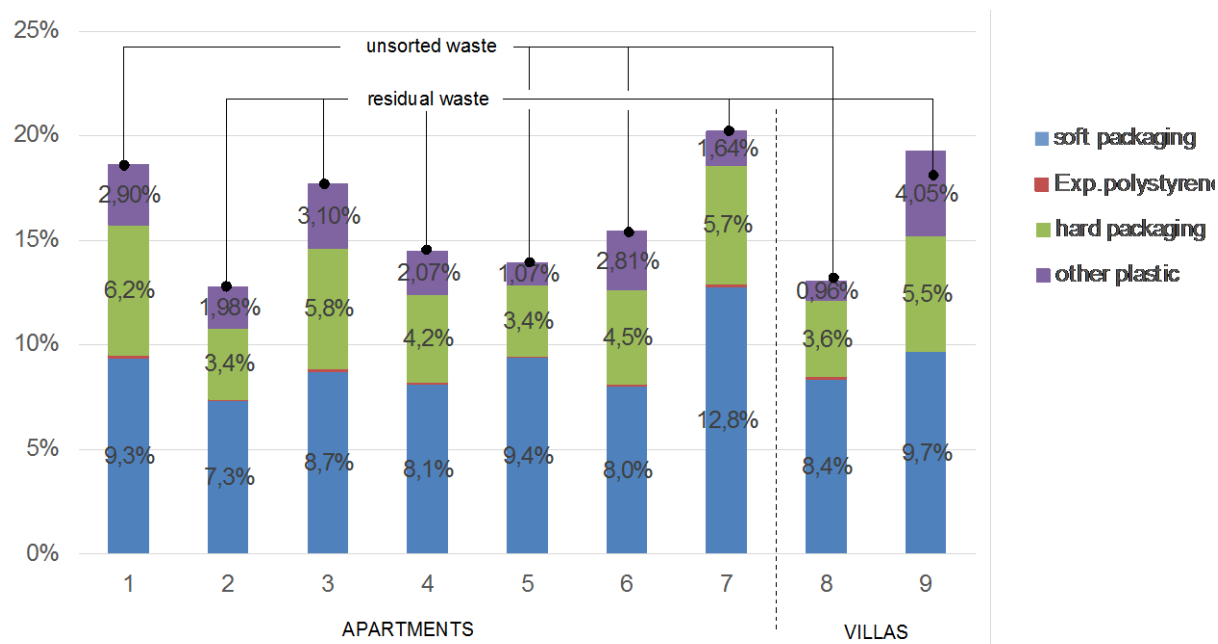


Figure 4: Fractions of soft plastic packaging, hard plastic packaging as well as other plastic in the analyses provided in (Kretslopp & Vatten, 2015).

By averaging such values for apartments and villas and for unsorted and residual waste, the following fraction streams were estimated for year 2010:

- soft packaging : 110 kt;
- hard packaging: 53 kt;
- other plastic: 30 kt.

The amount of packaging in the household waste is therefore revised from 151 kt shown in Table 3 to 163 kt and the amount of other plastic from 42 kt to 30 kt.

From the report by University of Luleå (Dahlén and Vukicevic, 2009) it was then possible to acquire more data about the actual mix of polymer types that typically constitute soft and hard packaging as well as other plastics.

This report presents sample analyses on sorted recycled packaging in the cities of Helsingborg and Malmö in year 2009 and the results are here reported in Table 5.

Table 5: Polymer composition of hard and soft plastic packaging and other products in the sorted recycled plastics according to sample analyses reported in (Dahlén and Vukicevic, 2009, figure 11, page 16).

Plastic type	PET	HDPE	PVC	LDPE	PP	PS	other	sum
hard plastic packaging	25%	25%	3%	2%	35%	10%		100%
soft plastic packaging		10%		42%	10%	15%	23%	100%
other products	1%	3%	4%	15%	55%	13%	9%	100%

We decided to use these values for estimating the final distribution of plastic resins in the unsorted waste in absence of other data but we are aware that different polymer types constitute different products which may end up more or less easily in the sorted plastic stream (i.e. to material recycling) rather than in unsorted waste. Such assumption introduce a large uncertainty.

Note that the portion of soft plastic that is “other” is rather high (23%). This portion was assumed to be PA which is also commonly used in soft packaging. Conversely the “other” portion in other products was assumed to be equally distributed into other relevant plastic types (PUR, ABS, PC, PMMA, PA).

The amount of plastic in the sorted food waste appears to be negligible or within the possible uncertainty margins so it was neglected in further calculations.

The plastic in the so called bulky waste, the waste from municipal garbage bins for instance, consists of about 50% PP, 30% PE (Fråne et al., 2012). It was decided to divide the remaining portion (i.e. 20% of the plastic in the bulky waste) in 25% PVC, 25% PS, 25% PET, and 25% PA.

From the above information about composition it was then possible to calculate the waste streams of plastic types from the residential sector as show in Table 6.

Based on the above mentioned assumptions, the total amount of plastic waste stream from the residential sector that can potentially be sent to chemical recycling is estimated to be around 230 kt per year. Taking into account the average composition this corresponds to a chemical energy content of around 2 670 GWh per year from the residential sector.

Table 6: Calculated flows of plastic waste from residential sector (excl. sorted plastic packaging and sorted deposit bottles) by polymer types.

Plastic resins	Plastic packaging in the residual waste (t/y)	Other plastic in the residual waste (t/y)	Bulky waste (t/y)	Total (t/y)
HDPE	24 250	900	5 400	30 550
LDPE	47 260	4 500	5 400	57 160
PP	29 550	16 500	18 000	64 050
PVC	1 590	1 200	1 800	4 590
PS	21 800	3 900	1 800	27 500
PET	13 250	300	1 800	15 350
PUR	-	540	-	540
ABS	-	540	-	540
PC	-	540	-	540
PMMA	-	540	-	540
PA	25 300	540	1 800	27 640
Total	163 000	30 000	36 000	230 000

2.3.1.2 Construction and demolition sector

According to the data in (Fråne et al., 2012) which were collected from (Yaramadi, 2003) and from SWEREC, more than 50% of the plastic resin in the construction sector is PVC, the remaining fraction being mainly PS, by PE and PP. PUR is also a common resin used in insulation.

The following assumptions were made about composition of the plastic waste stream from this sector: PVC (60%), PS (10%), PP (10%), PUR (10%), HDPE (5%), LDPE (5%).

From the above information about composition it was then possible to calculate the waste streams of plastic types from the construction and demolition sector as show in Table 7.

The estimated total amount of plastic waste stream from the residential sector that can be potentially sent to chemical recovery is around 43 kt per year.

The total chemical energy rate in the calculated plastic waste stream from the residential sector amounts to around 340 GWh.

Table 7: Calculated flows of plastic waste from construction and demolition sector (excl. sorted plastic) by polymer type.

Plastic resins	(t/y)
HDPE	2 150
LDPE	2 150
PP	4 300
PVC	25 800
PS	4 300
PET	-
PUR	-
ABS	-
PC	-
PMMA	-
PA	-
Total	43 000

2.3.1.3 Manufacturing and services

The amount of plastic waste from manufacturing and services sector is the second largest stream after the residential sector. The quantity estimated in Table 8 is based on more precise data declared by companies, however data about composition of such plastic were not found.

Table 8: Calculated flows of plastic waste in sorted plastic waste from manufacturing and services by polymer type.

Plastic resins	(t/y)
HDPE	10 560
LDPE	14 960
PP	16 720
PVC	10 560
PS	7 040
PET	5 280
PUR	6 160
ABS	4 180
PC	4 180
PMMA	4 180
PA	4 180
Total	88 000

Accordingly it was decided to assume the distribution of plastic resin similar to the European average (see table 2 in (Fråne et al., 2012)): PP (19%), LDPE (17%), HDPE (12%), PVC (12%), PS (8%), PUR (7%), others (19%). The percentage of other plastic resins was distributed evenly into: ABS (4.8%), PC (4.8%), PMMA (4.8%), PA (4.8%).

From the above information about composition it was then possible to calculate the waste streams of plastic types from manufacturing and services as show in Table 8.

The estimated total amount of plastic waste stream from the manufacturing and service sectors that can potentially be sent to chemical recovery is around 88 kt per year.

The total chemical energy rate in the calculated plastic waste stream from manufacturing and services is around 922 GWh per year.

2.3.1.4 Medical applications

The amount of plastic in the medical waste in year 2010 was about 13 kt (Fråne et al., 2012). Since there are not data about composition of such plastic waste, it was decided to take the distribution of plastic resins in the market as done for the plastic waste from manufacturing and services.

From the above information about composition it was then possible to calculate the waste streams of plastic types from manufacturing and services as show in Table 9.

The total chemical energy rate in the calculated plastic stream in medical waste is around 140 GWh per year.

Table 9: Calculated flows of plastic waste in sorted plastic waste from medical application by polymer type.

Plastic resins	(t/y)
HDPE	1 560
LDPE	2 210
PP	2 470
PVC	1 560
PS	1 040
PET	780
PUR	910
ABS	618
PC	618
PMMA	618
PA	618
Total	13 000

2.3.1.5 Electronic waste

Stena Metall provided the ultimate analysis of electronic waste shown in Table 2. The total amount of electronic waste handled by Stena is around 10 kt per year of which half is sent to energy recovery, half is sent to landfill. Since the plastic in electronic waste ends up mostly in the fraction sent to energy recovery. The amount of plastic in electronic waste sent to energy recovery reported in (Fråne et al., 2012) for year 2010 was about 13.5 kt, which indicates that other sources of electronic waste than those handled by Stena Metall exist.

As already discussed in the introduction, it was decided to retain the whole WEEE for thermochemical recycling and not only the plastic fraction since the idea is to process this metal rich waste stream in a pyrolysis plant with integrated metal recovery.

If the ultimate and proximate analyses provided by Stena Metall are extrapolated, this means that the whole amount of WEEE that can be potentially sent to thermochemical recycling process is about 16 600 t, being 13 500 t only the organic dry part which is about 81% of the total waste as received.

Using the calculated HHV reported in Table 2, the total chemical energy rate in the calculated WEEE stream amounts to around 125 GWh.

2.3.1.6 Automotive sector

There are two main flows of vehicles that are demolished: those that reached the end-of-life and those that have been taken under responsibility of insurance companies after accidents. Some plastic components in this latter type of vehicles are recycled as reserve components for other vehicles. Most of the vehicles are instead demolished and the largest part of plastic ends up in the so called “shredder light fraction” (SLF).

With the current handling technologies, the largest portion of SLF is sent to energy recovery, the remaining part is sent to landfill.

Similarly to WEEE, it appeared relevant to include the whole amount of SLF to be sent to thermochemical recycling and in particular to a pyrolysis process with integrated metal recovery. Note that, compared to electronic waste, which organic part is substantially plastics (between 40 to 45% of dry matter), ASR-SLF consists also of wood and textiles (about 15% of dry matter), and rubbers (about 10% of dry matter). Retaining the whole organic fraction in SLF for subsequent chemical recycling can be seen as a case of co-gasification of biomass and plastics and it is therefore in line with the scope of the work.

The total amount of SLF handled by Stena is 65 kt per year. The estimated corresponding plastic stream in SLF is about 25 kt per year which is larger than the total amount of plastic reported in (Fråne et al., 2012).

According to the HHV calculated based on the ultimate analysis of SLF provided by Stena Metall, the corresponding total chemical energy rate associated with the SLF waste stream is around 238 GWh per year.

2.3.2 Summary of plastic waste streams and potential for chemical recycling

Table 10 shows the estimated total amount of plastic waste stream in the Swedish waste stream that was sent to energy recovery, incineration or landfilling in Sweden and that potentially be sent to thermochemical recycling.

Considering that chemical recycling should be complementary to material recycling it was decided to consider a future scenario where the fraction of plastic sent to material recycling is increased. Based on indications from Stena Metall, this will interest particularly some plastic resins, such as polyolefins, for which separation technologies with fairly good selectivity already exist. In addition, it appears reasonable that such advancements in material recycling are implemented for those waste streams consisting predominantly of polyolefins.

It was therefore decided to allocate 75% of the polyolefins (HDPE, LDPE, PP) of the household sector, manufacturing and services to material recycling in a more sustainable future scenario, which leaves only 25% of such polymers from these sectors for chemical

recycling. The whole plastic waste streams from the construction & demolition sector and the medical sector is instead considered for chemical recycling.

Note that portion of polyolefins in the medical sector may also be comparable to that of the household sector but is usually of a more dangerous nature and therefore may hinder similar material recycling rates.

In addition, 65 kt of ASR-SLF and 16.6 kt of WEEE are also included as input to the chemical recycling processes.

Table 10. Summary of estimated plastic waste streams generated in Sweden, by sector and by resins (excluding electronics and vehicle demolition), which are sent to energy recovery (incl. cement industry). Estimates are based on aggregated data for 2010. (only 25% of this value considered for chemical recycling)*

	Household	Manufact. & Services	Construct. & Demolition	Medical application	Total Sweden	To chem.rec.
HDPE (kt/y)	30.6*	10.6*	2.2	1.6	44.8	14.0
LDPE (kt/y)	57.2*	15.0*	2.2	2.2	76.5	22.4
PP (kt/y)	64.1*	16.7*	4.3	2.5	87.5	27.0
PVC (kt/y)	4.6	10.6	25.8	1.6	42.5	42.5
PS (kt/y)	27.5	7.0	4.3	1.0	40.0	40.0
PET (kt/y)	15.4	5.3	-	0.8	21.4	21.4
PUR (kt/y)	0.5	6.2	4.3	0.9	11.9	11.9
ABS (kt/y)	0.5	4.2	-	0.6	5.3	5.3
PC (kt/y)	0.5	4.2	-	0.6	5.3	5.3
PMMA (kt/y)	0.5	4.2	-	0.6	5.3	5.3
PA (kt/y)	27.6	4.2	-	0.6	32.4	32.4
Total (kt/y)	229.0	88.0	43.0	13.0	373.0	227.5

3 Overview of technologies for thermochemical recycling of plastics

In this section the process concepts and technological aspects of thermochemical recycling of plastics are briefly described.

For a more complete overview of feedstock recycling from plastics and in particular of the aspects of plastics pyrolysis the reading of the book by Scheirs and Kaminsky is highly recommended (Scheirs and Kaminsky, 2006). Some highlights from this book are reported in the following and further integrated with other references collected during a brief literature review.

Thermochemical recycling of plastics for feedstock recovery has been largely investigated in the past and few demonstration plants were also built as shown in Table 11. Note that in this table, among input waste streams, automotive shredder residues (ASR) and tyres were also included which are waste streams resulting from car demolition. As discussed later, ASR is a heterogeneous material rich in plastics but also in metal and may represent an interesting opportunity for an integrated feedstock and metal recycling (Viganò et al., 2010).

The processes fall into two large categories: pyrolysis and gasification.

Pyrolysis is the thermal decomposition of an organic substrate in absence of oxidation processes. This implies that either combustion does not occur for kinetic reasons or because heating of the substrate and decomposition occurs in oxygen-free atmosphere.

Gasification is the also a thermal decomposition of an organic substrate but differ from pyrolysis for the presence of a reforming agent, e.g. steam, which contributes to certain conversion of heavy hydrocarbons into lighter ones. The endothermic gasification reactions can be sustained either by indirect heating via heat exchange with e.g. a bed material, or by simultaneous partial combustion of the organic substrate or of the intermediate product of decomposition in which case an oxidation agent such as air or even pure oxygen is also used. Gasification usually implies higher temperatures and therefore the starting material is decomposed in a mixture of smaller compounds. The processes based on gasification generally decompose the substrate into syngas which can be used in downstream synthesis processes for production of chemicals or fuels.

Conversely, pyrolysis achieves a milder decomposition compared to gasification, and high value chemicals are obtained directly in the liquid or gaseous phase of pyrolysis products, thus simplifying the process chain to valuable product mix. In fact, different polymers can be converted into a large variety of products depending on process conditions (reactor type, catalyst, temperature, residence time). A pyrolysis process could be therefore tailored for a specific polymer in the input waste stream (e.g. LDPE) and a specific product (e.g. aliphatic hydrocarbon mix) (Scheirs and Kaminsky, 2006).

There is an increasing consensus that, if a specific polymer can be recovered, this should be in a material recycling fashion to achieve the highest degree of recycling. Accordingly, thermochemical recycling appears as a promising solution for processing mainly mixed plastics waste streams. In a development stage, due to the rather small scale of the plants, the preferred processes are therefore based on pyrolysis of mixed plastic waste for production of hydrocarbon mixtures which can be then processed in existing refinery or petrochemical facilities (Kaminsky et al., 2004).

Table 11: Examples of plants for feedstock recycling from plastic waste, adapted from (Scheirs and Kaminsky, 2006)

Company	Reactor type	Process type	Input	Output	Status
Akzo Nobel	Circulating fluidised bed	Fast pyrolysis, 700-900°C	Shredder Plastics (incl. PVC)	HCl, CO, H ₂ , CH ₄	Pilot (up to 400kg/h)
Amoco		Catalytic cracking, 500-600°C	PE, PP, PS	Naphtha	Pilot
BASF	Melting vessel	Liquid phase pyrolysis, up to 500°C	Plastic waste	Petrochemical feedstock	Demo (15kt/y)
Battelle	Circulating fluidised bed	Gasification, 900°C	PE, PS, PVC	Ethylene, H ₂ , CH ₄	Pilot (9 kg/h)
BP polymer cracking	Bubbling fluidised bed	Pyrolysis, 500°C	Mixed plastics (w/o PVC)	Petrochemical feedstock	Pilot (50kg/h)
Fuji	Extruder, fixed bed	Extrusion, catalytic cracking 400°C	Polyolefins	Gasoline, Kerosene, Diesel	Pilot, Demo (5kt/y)
Hamburg	Bubbling fluidised bed	Pyrolysis, 800°C	Plastic waste (w/o PVC)	Olefins, BTX	Pilot, Demo (5kt/y)
Mazda	Fixed bed	Catalytic cracking, 450°C	ASR	60% oil	Pilot (400t/y)
Swarze Pumpe		Gasification	ASR, tyres, MSW	Methanol, energy	
Veba Oel	Rotary kiln	Pyrolysis 500°C, Gasification >1000°C	ASR, tyres	Carbon-black, oil, gas	Demo (12t/h)

3.1 Plastic pyrolysis

As described in (Scheirs and Kaminsky, 2006), the processes of pyrolysis of plastics can be subdivided into four general categories: monomer recovery, non-catalytic low temperature pyrolysis, non-catalytic high temperature pyrolysis, catalytic pyrolysis.

Monomer recovery processes are substantially tailored for processing PMMA or PS at a temperature between 450 and 500°C usually in a nitrogen atmosphere. The major aim in this case is decomposing the polymer into a gas containing the corresponding monomer, respectively methyl-methacrylate (MMA), styrene.

The non-catalytic pyrolysis processes operating at temperature between 500 to 600°C can be grouped under the category of low temperature feedstock recovery. The aim is

decompose single polymers such as PE, PP, PS or PVC or mixed plastics into a mixture of hydrocarbons of different natures (aliphatic, olefins, etc.) in the C1 to C50 range. Pyrolysis occurs in nitrogen but steam can also be used which may partly contribute to secondary decomposition of the primary pyrolysis products.

Non-catalytic processes working at temperatures between 600 and 800°C can be grouped under the category of high-temperature feedstock recovery and usually convert polyolefins, PS or PVC into a gas which can be partially condensed into a BTX rich oil. The non-condensable gas is often partially recycled into pyrolysis to create an oxygen free atmosphere.

The addition of different types of catalysts, especially in case of fluidised bed pyrolysis, allows to convert certain polymers into a narrower range of hydrocarbons and products therefore greatly differ between different processes. The presence of catalyst also contribute to enhance the process kinetics which can either translate into lower temperatures (300 to 500°C) or shorter residence times.

Table 12: Overview of characteristics of different reactor types adapted from (Scheirs and Kaminsky, 2006). BFB: bubbling fluidized bed; CFB: circulating fluidized bed.

	Fixed bed	BFB	CFB	Rotary Kiln
<i>T profile</i>	Large	T constant	Follows mass transfer	Large
<i>T range</i>	400 – 800 C	500 – 850 C	750 – 850 C	450 – 800 C
<i>Heat transfer</i>	Poor	Very good	Very good	Poor
<i>Particle size</i>	Wide range / large	Med. diam: 3 mm	< 10 cm	Large
<i>Res. Time</i>		Min / hours	Follows recirculation	1 – 2 hours
<i>Conversion</i>	High conv. Possible	Poor	High conv. Possible	High conv. Possible
<i>Feedstock flexibility</i>	Poor	Excellent	Excellent	Limited
<i>w/o Catalyst</i>	Unsuitable for continuous operation	Excellent	Excellent	Very good with large solid content
<i>w Catalyst</i>	Slow	Excellent		
<i>Scale-up</i>	Poor	Limited	Limited	
<i>Cost</i>	High	Moderate at large scale	Like BFB	Maintenance high!

Temperature and residence time can lead to different product characteristics depending on the substrate. Generally high temperatures allow to obtain larger quantities of gas while more solid product, char and waxes are obtained at low temperatures. Temperature has also a significant effect on the type of hydrocarbons in the products: aromatic compounds

tends to result from decomposition of polyolefins at high temperatures and from PS at low temperatures.

In addition to temperature, catalyst, and residence time, the type of reactor is also critical for determining the characteristics of the pyrolysis products. Table 12 gives an overview of different reactor types.

The research in pyrolysis appears to favour fluidised bed technology since it guarantees the best conditions for temperature control due to the excellent heat transfer, for feedstock flexibility and it is very suitable to addition of catalysts. Circulating fluidized bed can be used to achieve high conversion also with moderately large particle size.

Still, rotary kiln type of reactors is common in demonstrated or commercial plastic pyrolysis plants since it requires lower investment compared to circulating fluidized bed technology although maintenance cost may be higher. An advantage of rotary kiln reactors is the possibility of processing material with relatively high content of inert solids. These characteristics makes rotary kiln particularly suitable for processing highly heterogeneous material such as ASR, WEEE or MSW where large amount of solid product containing char, metals and inorganic material is obtained. A downside of rotary kiln reactors is however the long residence time required to obtain a good conversion.

3.1.1 Selected papers

3.1.1.1 *Pyrolysis of single polymers or mixed plastic*

Feedstock recycling via thermal cracking of various blends of PP and PS is discussed in (Angyal et al., 2007). The experimental trials were conducted in a horizontal tube reactor at around 500°C and with residence time between 15 and 30 min. PS was found to increase the reaction rate and the conversion of PP. PS also contributes to increase light hydrocarbons and aromatics in the naphtha range. The liquid product has good characteristics for utilization as petrochemical feedstock.

The pyrolysis of PS is discussed in (Williams et al., 1993), where results from thermal degradation at temperature between 500 and 700°C in a batch reactor are shown. PS produces large amount of styrene oligomers and polycyclic aromatic compounds (PAH) which appear to further increase with secondary cracking in zeolite catalyst.

Detailed results of catalytic thermal degradation of single polymer such as LDPE, HDPE and PP at 450°C are presented in (Achilias et al., 2007). The obtained gas and liquids contain considerable amounts of aliphatic compounds which are suitable for utilization as petrochemical feedstock.

The non-catalytic pyrolysis of single polymers such as PE, PP and PS for production of gasoline range hydrocarbons is also discussed in (Demirbas, 2004). It was found that liquid yield is generally higher for PS while gases are more abundant in case of PE and PP. BTX can be produced after subsequent upgrading of the liquids with styrene being the main compound of PS degradation.

The fluidised bed pyrolysis of LDPE is discussed in (Williams and Williams, 1999). Experiments were conducted for different temperatures between 500 and 700°C. It was found that the gas contain mainly hydrogen, methane, ethane, ethane, propane, propene, butane, butane. The derived oils and waxes contain mainly aliphatic compounds but the presence of aromatics was found to increase dramatically with the temperature.

Results of pyrolysis of PE are presented in (Bagri and Williams, 2002). The experiments were conducted between 400 and 600°C without catalyst and aliphatic compounds were

mainly found in the oil product. By addition of zeolite catalyst a remarkable increase in aromatic compounds was found which also increase with the temperature.

Results of pyrolysis of PE, PS and their mixture in a closed batch reactor between 300 and 500°C are presented in (Onwudili et al., 2009). The decomposition of PS leads to high amount of aromatics which are mainly converted into char with increasing temperature. The increase of temperature of PE pyrolysis leads mainly to increase of the gas fraction. PS appears to have a catalytic effect also with PE since pyrolysis of mixture of PE and PS have lower initial degradation temperature and produces generally more oil and less char.

Non-catalytic pyrolysis of PE in a laboratory tube reactor between 400 and 500°C is also discussed in a more recent publication (Kumar and Singh, 2013) where more detail analysis of the liquid products is shown. The pyrolytic oil was found to contain a large variety of chemical groups: alkane, alkenes, alcohols, ethers, carboxylic acids, etc. The physical properties of the oil were found however quite close to a mixture of petroleum products.

Large experience on pyrolysis of PE, PP, PS and PMMA as well of mixed plastics and MSW has been collected by University of Hamburg where fluidized bed pyrolysis was successfully demonstrated. In (Kaminsky et al., 2004) monomer recovery from PMMA and PS is described. The article also gives a short overview of the other activities around the Hamburg process: low temperature pyrolysis of plastics for production of oil and waxes that may serve as feedstock for steam cracker; high temperature pyrolysis of plastic waste optimized for production of olefins; high temperature pyrolysis with recirculation of liquid-free pyrolysis gas for secondary cracking optimized for production of BTX.

Detailed analysis of pyrolytic oils obtained from a pilot pyrolysis plant in South Korea processing mixed plastic waste obtained as discarded fraction of a material recycling unit (Sep and Shin, 2002). The plastic waste was composed by about 50 to 60 % PE, 20 to 30% of PP, 10 to 20% of PS and about 10% of PVC. The distilled oil contained much more aromatics than commercially available petroleum oil.

Thermal degradation of ABS is discussed in (Suzuki and Wilkie, 1995) and it was found that is similar to decomposition of its constituent. The composition of oils obtained from ABS degradation between 360 and 440°C is discussed in (Brebü et al., 2000). It was found that at 440°C, around 60% of the initial ABS is recovered in the oil and the oil has large amount of Nitrogen-containing compounds mainly aliphatic and aromatic nitriles and pyridine.

A particular attention deserve the pyrolysis of PVC since Chlorine containing products are particularly detrimental to any equipment especially at high temperature. In (Bockhorn et al., 1999), dehydrochlorination of mixed plastics by thermal degradation at around 330°C is demonstrated. Similarly, brominated flame retardants are also released at temperature just higher than 300°C which also can be a practical way to prevent formation of highly contaminating compounds from pyrolysis of plastic mixtures from electronic waste.

3.1.1.2 Pyrolysis of automotive shredder residues

Experimental trials of ASR pyrolysis in rotary kiln reactor are presented in (Day et al., 1999). The temperature of the reactor was varied between 500 and 750°C. The hydrocarbon yields increased progressively from 60 to 85% of the input organic fraction with increasing temperature. However, at lower temperature heavy hydrocarbons are obtained. Larger quantities of aliphatic compounds are obtained at low temperatures and more aromatics are found at higher temperatures.

Results of pyrolysis of light and heavy ASR (respectively with low and high content of inorganics) in a 3.5 litre autoclave reactor at temperature between 400 and 700°C are reported in (de Marco et al., 2007). A promising product range was obtained for heavy ASR: valuable solids (around 40%), liquid (between 20 and 30%) and gases (around 30 to 40%).

Large amount of inorganics (up to 55%) make instead the product of pyrolysis of light ASR quite poor. 500°C appear a sufficiently high temperature for decomposition of the organic part of ASR.

Results from experimental trials on a pilot plant for ASR pyrolysis in Italy are discussed in (Galvagno et al., 2001). Temperature was varied between 550 and 680°C and the product fractions varied as follows: char (60 – 40 %), oil (20 - 30%), gases (4 – 13%).

A recent review on ASR pyrolysis is available in (Harder and Forton, 2007). The authors conclude that ASR is highly heterogeneous and processes are difficult to standardise. This makes ASR pyrolysis technology on its own less attractive than processes where ASR is co-pyrolysed with other waste streams.

3.1.1.3 Pyrolysis of electronic waste

Recycling of WEEE has received quite large attention in the recent years.

Pyrolysis of different electric and electronic waste is discussed in (de Marco et al., 2008). Among the processed input streams were PE wires, table phones, mobile phones, and printed circuit boards, which cover a broad spectrum of possible composition of WEEE. The pyrolysis trials were conducted in 3.5 litre autoclave reactor at 500°C for 30 min. PE wires yield mostly liquids, phones yield mostly a brown coloured fluid liquid together with large amount of char, while printed circuit boards leave mainly a solid fraction. The article focuses mainly on recycle of metals which appears completely feasible while the gaseous and liquid products are mainly considered for energy purposes, e.g. for sustaining the process.

The pyrolysis of printed circuit boards is also discussed in (Jie et al., 2008) where metal recycling is also considered as the primary objective and the gaseous product is used mainly for sustaining the process itself.

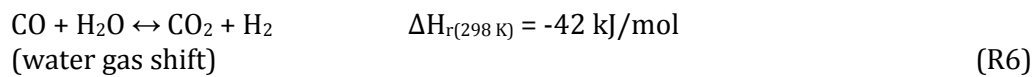
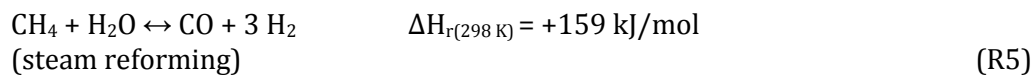
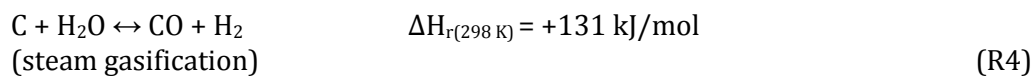
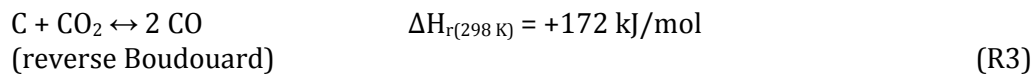
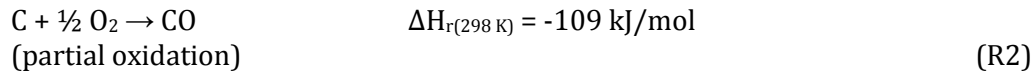
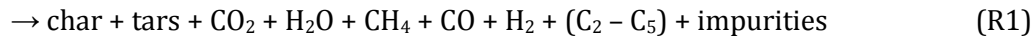
Detailed results of analysis of combustion and pyrolysis of electronic waste are discussed in (Moltó et al., 2009) where emphasis is put on detecting halogenated compounds and in particular on the fate of Bromine originated from brominated flame retardants.

Different dehalogenation techniques are reviewed in (Yang et al., 2013).

3.2 Gasification

Thermal gasification of any fuel basically proceeds in three major steps. First the (remaining) fuel moisture is evaporated, followed by pyrolysis converting the biomass into a char as well as permanent and condensable (water and tars) gases. Finally, char is (partially) converted to gaseous products and gas phase reactions take place during the gasification step. The major chemical reactions occurring in gasification are listed here (adopted from Heyne et al. (2013)):

Biomass feedstock \rightarrow



The first reaction (R1) represents the pyrolysis step while the remaining reactions (R2-R6) are heterogeneous and homogeneous gasification reactions, respectively.

The various gasification technologies considered for realizing these conversion reactions require specific feed qualities, have different ranges of operation, and – most importantly – have a certain range of capacity. Indicative values for these different parameters are given in Table 13. Fixed bed gasification is mainly suited for small scale applications, whereas fluidised bed and entrained flow gasification are more suitable for medium to large scale applications.

Table 13: Gasification technology characteristics.

	Fixed Bed	Fluidised Bed	Entrained Flow
Input Particle Size [mm]	10 – 300	< 50	< 0.1
Outlet Gas Temperature [°C]	400 – 1000	700-1200	1200-1500
Operating Pressure	from atmospheric pressure (1 bar) to ~25 bar		up to 80 bar
Gasification Medium	air, steam, oxygen, flue gas, product gas		
Plant Size [MW _{th} input]	< 10	10 – 200	100 – 1000

The different operational ranges and setups also result in differing qualities of the product gas with respect to gas composition, heating value and level of purity (e.g. tar content). Besides the gasification technology, the gasification medium influences these properties to a major extent. Fixed bed and entrained flow gasification are direct gasification technologies with an oxidising medium (e.g. air or oxygen) partly combusting the biomass in order to provide the necessary heat for gasification. Fluidised bed gasification can be operated in the same way using oxygen for direct gasification, but even allows for indirect gasification, with

the heat for gasification being transferred to the biomass by means of the circulating bed material. A separated combustion chamber then heats up the circulating bed particles. The non-gasified char from the gasification reactor provides additional fuel supply to the combustion chamber. Indirect gasification produces a gas with very low nitrogen content, lower CO₂ content compared to direct gasification as the combustion is conducted in a separate chamber, but is more difficult to operate under pressure (limiting scale-up). Its advantage within the context of syngas production for downstream synthesis is that no air separation unit for oxygen production is needed. In the case of direct gasification, oxygen-production is necessary in order to obtain a nitrogen-free gas. Entrained flow gasification is the technology for the high-end of thermal input (up to the GW range) but needs pretreatment in case of biomass, such as pyrolysis or torrefaction in order to obtain a liquid or grindable feedstock. It has been applied to black liquor gasification within the pulp and paper sector.

3.2.1 Biomass gasification

Biomass gasification has been investigated within several contexts; production of renewable transportation fuels, conversion of pulp mills to biorefineries, production of green chemicals and materials within the chemical industry, are some of the more prominent sectors that have been and still are relevant for biomass gasification applications.

The development of biomass gasification is a continuation of coal gasification research being of high interest during the oil crisis in the 1970ies, for example. Striving for CO₂ emission reductions was the major driving force for the recent biomass gasification activities. A number of pilot and demonstration plants have been build and are operating, large scale plants often not being realised due to economic constraints, the low price level for fossil feedstock not allowing for economic profitability. Among the demonstration plants, the Güssing plant in Austria based on indirect gasification is a prominent example. Based on the Güssing technology a number of down-stream synthesis processes have been demonstrated, such as synthetic natural gas (SNG) or FT-Diesel production.

In Gothenburg, Göteborg Energi built a 20 MW_{SNG,LHV} gasification plant (GoBiGas project phase 1) similar to the Güssing concept that currently is in operation. At Värnamo in Sweden, direct gasification of biomass for power generation was demonstrated and the plant was mothballed in 2000. A number of projects for downstream synthesis of biofuels have been planned since then, but the plant has not been taken back in operation so far (Ståhl 2001, Waldheim 2012). Entrained flow gasification of black liquor for production of DME and/or methanol was demonstrated by Chemrec in Piteå, Sweden. There are a number of large scale projects in Sweden such as GoBiGas phase II, Bio2G, Värmlandsmetanol that have come to quite a detailed stage of planning but that are on hold due to economic uncertainties related to biofuel policies and investment support. Technically, biomass gasification is rather mature, the major development areas being tar cleaning/reforming and scale-up that still are topics of research activities in order to cut down costs for the biorefinery concepts. Biomass-based processes often are competing with fossil counterparts (in chemical or refinery industry) that often exceed the scale by a factor of about 10 leading to a tough challenge for bio-based processes of matching the economic performance of fossil alternatives without any subsidies.

3.2.2 Plastic gasification

Since 1990 a number of studies have been starting to investigate concepts for plastics gasification, with the major aim to improve the recycling rate of plastics and move from energy recovery or even landfill to more sustainable tracks (Sharp & Ness 1991, Zevenhoven et al. 1997, Tukker et al. 1999, Pinto et al. 2002). A number of pilot plants have been established and are under operation (see Table 11). Often plants use the syngas produced from gasification for energy purposes at first hand but run pilot tests for future options for synthesising chemicals and materials. Enerkem has a large scale MSW plant in operation producing methanol/ethanol from waste (Chornet, 2014). The plant has a capacity to treat 100 000 t_{dry} refuse-derived fuel per year, producing up to 38 000 m³/y of ethanol.

Plastic gasification has quite different resulting gas composition compared to biomass gasification due to the high volatile fraction of the feedstock. In general, plastic gasification results in higher methane and light hydrocarbons yields, but also gives higher tar contents in the product gas (Wilk & Hofbauer 2013a, b). Char formation does occur in plastic gasification as it does in biomass (or coal) gasification, but the mechanisms for formation are substantially different. A number of studies investigated the differences between plastic and biomass gasification as well as potential synergies when gasifying a mixture of plastics and biomass (Pinto 2002, Wilk & Hofbauer 2013a, b). Wilk & Hofbauer (2013a, b) present positive effects on the reduction of tars while maintaining relatively high methane and ethylene yields when gasifying mixed biomass and plastic feedstock.

With respect to waste streams – that are in focus within the present project – a plastic fraction that can be problematic for gasification is PVC, leading to substantial contents of HCl in the product gas. Different concepts for pre-treatment of PVC-containing plastic streams exist (VinylPlus 2015). From cable waste streams a number of material recovery concepts have evolved, such as the Vinyloop, Stigsnæs or Watech process (Kreißig et al. 2003). Another option proposed in literature is thermal pretreatment for dehydrochlorination by low-temperature pyrolysis (e.g. Bokhorn 1999). The latter process has been adopted within this project as HCl may be a potential feedstock for one of the Stenungsund chemical companies.

3.3 Syngas upgrading

The word “syngas” is commonly used to address a mixture of CO, H₂ which can also include CO₂, water, and traces of hydrocarbons.

In this work syngas is obtained from pyrolysis or gasification of organic substrate. However, syngas as a commodity in the refinery and petrochemical industry is usually obtained by reforming of hydrocarbons, such as natural gas, in steam reformers, autothermal reformers or partial oxidation units. Large quantity of syngas are also obtained from coal gasification. Syngas can also be obtained by blending of sequestered CO₂ with H₂ produced from renewable resources.

From H₂ and CO a large variety of chemicals can be produced. A thorough review of synthesis options from syngas, which are here summarised in Figure 5, is given in (Wender, 1996). Overall the production of the chemicals shown in Table 14 is reviewed in (Wender, 1996).

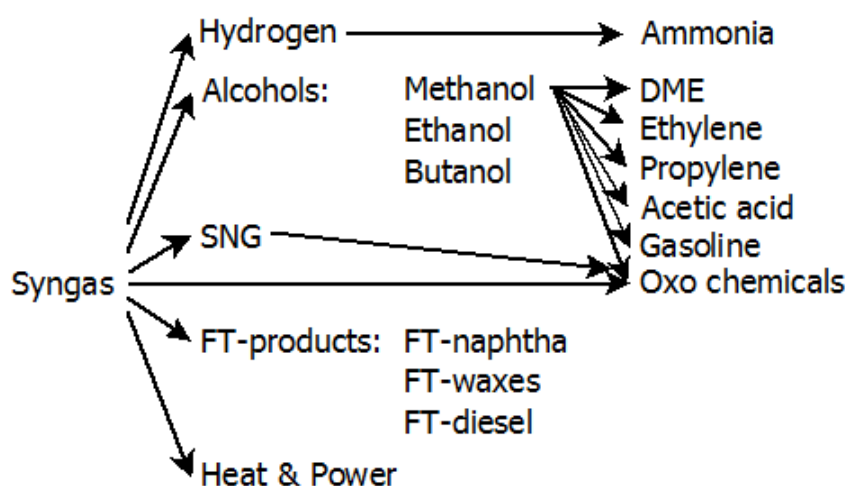


Figure 5: Overview of synthesis routes from syngas.

Table 14: Overview of commercial chemical production routes from syngas, adapted from (Wender, 1996).

Direct routes	Indirect routes via methanol or DME	Miscellaneous
<ul style="list-style-type: none"> . Hydrogen . Methanol . Ammonia . Carbon monoxide . Medium BTU gas . Methane (SNG) . Higher (C1-C6) alcohols . FT Gasoline . FT Diesel Fuel . Isobutanol . Isobutane 	<ul style="list-style-type: none"> . Formaldehyde . Acetic Acid . Methyl acetate . Acetic anhydride . Vinyl acetate . Methyl formate . Formic acid . Ethanol . Dimethyl carbonate . Dimethyl oxalate . Gasoline . Diesel Fuel . Ethylene . Propylene . BTX . Chloromethanes . Methylamines . Methyl glycolate . Ethylene glycol 	<ul style="list-style-type: none"> . Aldehydes / Alcohols via (olefins + syngas) . MTBE via (isobutylene + methanol and H₂) . Acrylic acid via (acetylene + H₂) . Highly branched acids via (Olefins + syngas) . RCH₂COOH via (RCOOH + syngas) . Isocyanates via (nitroaromatics + CO) . Dimethyl terephthalate via (terephthalic acid + methanol)

It should be noted therefore that when syngas is available, methanol or DME is a particularly interesting chemical platform, to the point that the idea of complete chemical clusters based on methanol was advanced in the past (Olah, 2005).

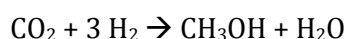
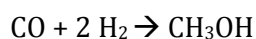
An exhaustive presentation of the various chemical production routes is beyond the scope of this report. In the following the main routes from syngas so far considered for the Stenungsund chemical complex site are presented. Note that these were the preliminary routes suggested for the utilization of syngas from plastics and biomass gasification although the production of ethanol from methanol was finally prioritized as discussed in chapter 4.

3.3.1 Synthesis routes from syngas considered in previous works for the Stenungsund chemical complex site

3.3.1.1 Methanol production and methanol to olefins

The production of methanol via biomass gasification was investigated in detail in the recent Skogskemi project (Joelsson et al., 2015). The reader is in particular referred to the report by Morandin and Harvey for more detail about the mass and energy balances around the biomass-to-methanol system (Morandin and Harvey, 2014).

Methanol can be synthesized from a CO and CO₂ according to the following reactions:



The production of methanol via gasification of biomass can reach a conversion on energy basis between 45 to 55% according to (Hamelinck and Faaij, 2002) but 60% conversion was also estimated based on rather advanced gasification process (Hannula and Kurkela, 2013).

The process for production of olefins via methanol is commonly referred to as methanol-to-olefins (MTO) and is one of the possible alternatives of the methanol-to-hydrocarbons routes based on the FCC technology for which a review is available in (Keil, 1999).

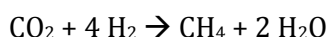
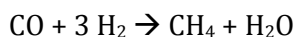
In the recent Skogskemi project the large scale production of olefins via MTO for the Stenungsund chemical complex was also investigated and preliminary results are also discussed in (Arvidsson et al., 2015a) which was based on previous master thesis work by Johansson (JOHANSSON, 2013). Methanol is firstly converted into DME and DME is then converted into a mixture of olefins and other hydrocarbons according to quite complex reaction path (Vora et al., 2001). The reactions can be somewhat adjusted to produce different olefin mixes (e.g. high ethylene, high propylene). It was found that the high propylene case has probably a better chance to be integrated at the Stenungsund chemical complex site. Overall 85% conversion on energy basis from methanol to raw olefins can be reached.

Raw olefins can be blended with olefins coming from existing steam cracker facilities which allow for significant capital investment savings compared to a stand-alone bio-olefins plant since the existing separation units can be utilized.

3.3.1.2 Synthetic natural gas (SNG)

SNG production via biomass gasification at the Stenungsund was investigated in (Arvidsson et al., 2012), for a process that is very similar to the process layout of the existing GoBiGas Bio-SNG plant in Gothenburg (Heyne, 2013).

SNG can be synthesized from CO and CO₂ according to the following reactions:



The conversion from biomass to SNG can reach values between 65 to 70% on energy basis.

Natural gas is used at the Stenungsund chemical complex site for two main purposes: as fuel in steam boilers and as feedstock for syngas production in partial oxidation units where the syngas is used for production of aldehydes.

3.3.1.3 Syngas to OXO synthesis

Since natural gas is used for production of syngas at the Stenungsund chemical cluster, it is quite obvious that such syngas could be produced directly from biomass without taking the detour through methanation. The opportunity of producing syngas for OXO-synthesis directly from biomass and its comparison to the bio-SNG routes are discussed in (Arvidsson et al., 2014) and (Arvidsson et al., 2015b).

One of the advantage of avoiding the methanation step relies on the fact that the H₂:CO ratio of syngas prior methanation should be around 3 which normally implies that water-gas shift must be employed to increase the share of hydrogen in the syngas which causes some carbon to be shifted into CO₂ and subsequently removed. Conversely, the syngas for OXO synthesis application has a H₂:CO ratio around 1 which facilitates the usage of syngas from biomass gasification.

It was found that the direct syngas production can lead to about 5 to 10 percentage points increase compared to the bio-SNG route on energy basis with significant benefits from GHG emission and economic standpoints.

4 Methodology

4.1 Definition of a calculation basis

The interest of the Stenungsund chemical companies is to develop a feedstock recovery process with high flexibility of processed waste streams. Accordingly, in addition to mixed plastic waste, ASR, WEEE, we have included among the inputs a given quantity of forest residues with the characteristics already introduced in Table 1 and Table 2.

The amount of biomass was decided by fixing the total input chemical energy rate to 525 MW on higher heating value (HHV) basis. This corresponds to the value identified in the Skogskemi project (Joelsson et al., 2015) where only biomass was considered for production of methanol and olefins. This assumption allows making some comparisons between process concepts processing different materials but having similar scale.

Table 15 shows a summary of the input waste streams considered.

Table 15. Summary of input waste streams considered for feedstock recycling at the Stenungsund chemical complex.

	<i>Mixed plastic waste (Table 2)</i>	<i>ASR</i>	<i>WEEE</i>	<i>Forest residues</i>	<i>Total</i>
Quantity (kt/y)	228	65	17	510	820
Chemical energy in HHV basis (GWh/y)	2173	238	125	1656	4 192
Averaged (8000 h/y) chemical energy rate in HHV basis (MW)	272	30	16	207	525

4.2 Candidate products for Stenungsund chemical complex

The chemical complex in Stenungsund is largely based on olefins production, currently performed by steam cracking of fossil feedstock such as naphtha and ethane. Ethylene is the main chemical intermediate for a large number of chemicals mainly via ethylene-oxide and OXO-aldehydes and also at the basis of plastic production, mainly LDPE, HDPE and PVC. The olefin mix at the site is strongly dominated by ethylene and currently around 200 kt of ethylene are imported every year. Several recent projects have focused on the substitution of fossil ethylene with bio-based ethylene. So far two main routes have been considered: via dehydration of green-ethanol produced by fermentation of various sugar substrates, via methanol to olefins (MTO) process from methanol produced via synthesis from syngas obtained by biomass gasification (Joelsson et al., 2015).

Methanol and ethanol are two important intermediates for other products at the site. Methanol is used for transesterification of rapeseed oil into RME, one of the largest production of biodiesel in Sweden. Ethanol is also used for production of ETBE, a gasoline additive. In addition ethanol could be converted in other alcohols via acetaldehyde.

The chemical complex has also a large import of natural gas. This has two main utilizations: as fuel in boilers for steam production and as feedstock for production of around 170 kt per year of syngas with a H_2 to CO ratio of 1 for OXO-synthesis.

As investigated in previous projects, the production of steam by recovering excess heat from new thermochemical conversion processes (e.g. from cooling the syngas from gasification) represents an important process integration opportunity by reducing the natural gas import, a clear advantage of placing such processes in closed proximity of the existing chemical plants.

Table 16 shows the steam demands at different temperature and pressure levels of the six chemical plants at the Stenungsund site that are satisfied by natural gas boilers.

Table 16. Steam demands at the Stenungsund chemical complex site.

	85 barg, 485°C	40 barg, sat.	28 barg, sat.	20 barg, sat.	10 barg, sat.	6 barg, sat.	2 barg, sat.	1 barg, sat.
Flow rate (t/y)	75	50	6	3.6	18	10	38	12

4.3 Definition of process layouts

In principle, a large set of downstream processes could be generated starting from the characteristics of the products obtained from a specific thermochemical conversion technology and specific characteristics of the processed waste streams as already discussed in chapter 3.

Based on indication from the literature, we can expect that pyrolysis of the mixed plastic waste shown in Table 10 would require several parallel plants and would produce a complex mixture of gas and oils rich in aromatics due to the abundant presence of PVC and PS, and comparably smaller amounts of polyolefins with respect to the mixed plastic sampled usually considered in the literature.

The utilization of such product at the Stenungsund chemical complex site would probably require a further upgrade, such as hydrogenation, or further cracking. We realised that old naphtha steam cracker units could serve for such purpose and the idea has been included among the topic of another research proposal. This option was impossible to investigate in this project due to limited time and resources so the pyrolysis of mixed plastic waste was at the end discarded in favour of gasification. In addition, synthetic routes have already been explored in previous projects which seem to lead to production of the candidate products identified above with rather high selectivity.

The amount of the input plastic waste stream considered is large and we therefore focused our attention primarily on fluidised bed gasification technology. This was also justified by prior work at Chalmers University of Technology on biomass gasification and on integration of such biorefinery concepts with the Stenungsund chemical complex (Morandin and Harvey, 2014, Arvidsson et al., 2014). In addition, since we followed a quantitative approach based on process modelling, fluidized bed gasification resulted a much simpler choice compared to low temperature pyrolysis of mixed plastic waste stream for which a characterisation of yields and products appear unrealistic in absence of experimental evidences.

Pyrolysis was instead considered as the promising option for ASR and WEEE since integrated metal recycling can significantly improve the economics and environmental impact of recycling. For the two plastic and metal-rich waste streams, ASR and WEEE, we established a simple pyrolysis model following a semi-quantitative approach based on literature data on similar materials. From pyrolysis a complex mixture of hydrocarbons in

gaseous phase and a solid metal-rich residues are obtained. The pyrolysis gas is then sent to partial oxidation to convert all the hydrocarbons into syngas.

An overview of the waste streams considered as input to the proposed thermochemical recycling processes are shown *Figure 6*.

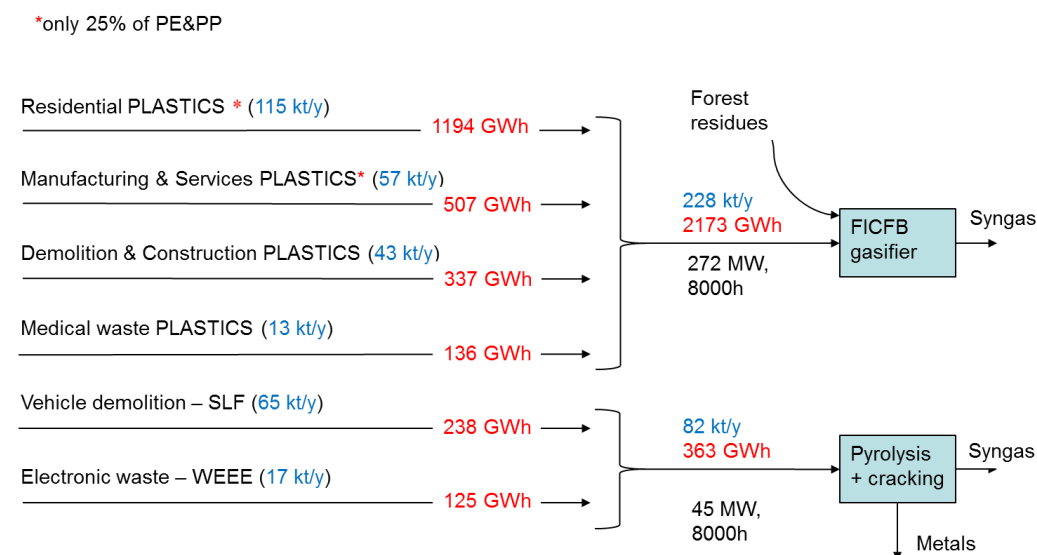


Figure 6: schematic representation of the waste streams considered as input to the two suggested thermochemical recycling processes.

Based on the $H_2:CO$ ratio of the syngas produced from gasification of mixed plastic waste and biomass, and of the syngas obtained from ASR and WEEE pyrolysis we have then devised two different downstream process layouts.

The first syngas has a $H_2:CO$ ratio around 2 which is convenient for methanol synthesis. The second syngas stream, of smaller amount, has a $H_2:CO$ ratio around 1 which is suitable for OXO-synthesis applications.

What remained left to decide, was to proceed from methanol to ethylene or at least olefins which can be recycled into plastic production. Since ethanol is also a candidate product, we have considered the route via methyl acetate to produce ethanol. This is similar to process layout adopted by Enerkem (Liu et al., 2013). Ethanol is then dehydrated into ethylene.

In summary the two following process concepts were outlined:

1. Mixed plastic waste and forest residue gasification, tar and CH_4 reforming, CO_2 separation, compression, methanol synthesis, methanol dehydration to DME, DME carbonylation into methyl acetate, methyl acetate hydrogenation into ethanol and methanol, methanol recovery, ethanol dehydration into ethylene. The basic layout of the process is shown in Figure 7.
2. ASR and WEEE pyrolysis with integrated metal recycling, partial oxidation of pyrolysis gas into syngas, syngas cooling and compression. The basic layout of the process is shown in Figure 8.

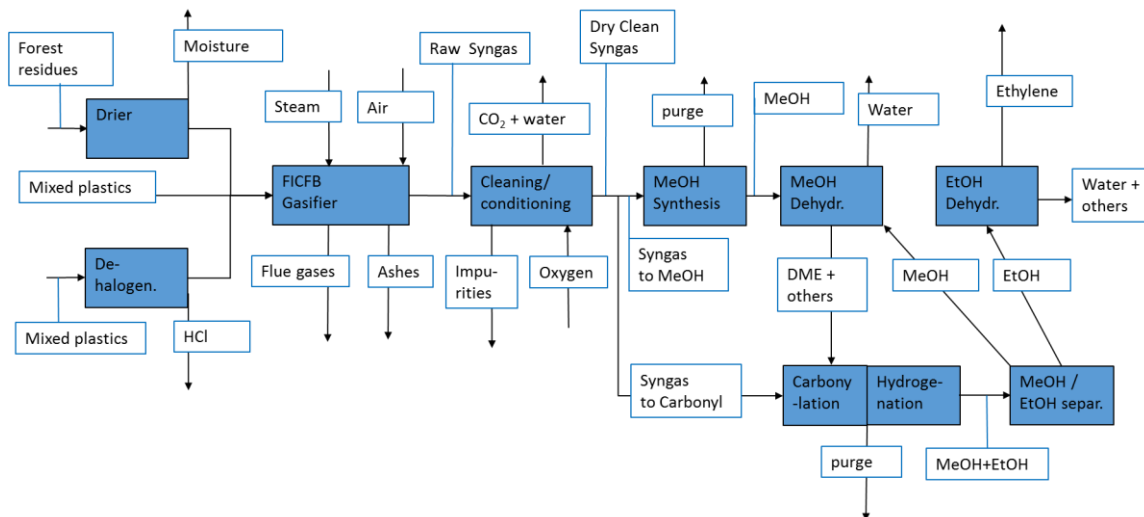


Figure 7: overview of the ethylene production process from gasification of mixed plastics and forest residues

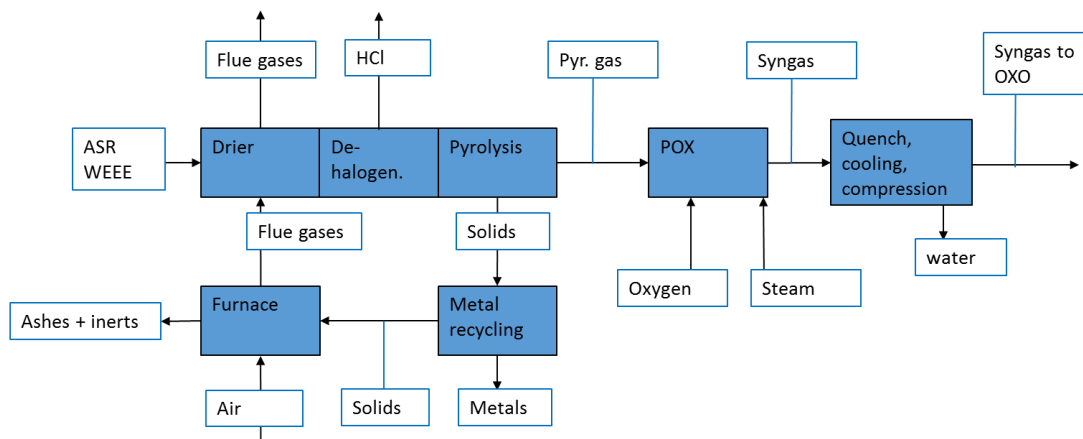


Figure 8: overview of process for production of syngas for OXO-synthesis applications

4.4 Process models

4.4.1 Biomass and plastic gasification

In order to cover the potential future scenarios on available plastic fractions and amounts, three different gasification concepts for syngas generation are taken into account in this study.

- Plastic only gasification
- Biomass only gasification
- Mixed plastic and biomass gasification

For all three gasification concepts it was aimed at scaling for a thermal input of 524 MW_{HHV} in order to make the results comparable to earlier studies focusing on biomass gasification only within the Skogskemi project (Joelsson et al. 2015) (450 MW_{LHV} of forest residues at 40% moisture content). The total amount of plastics per year (173 GWh_{HHV}) assumed available for chemical recycling as discussed in Section 2 however, results in a thermal input to the gasifier corresponding to 272 MW_{HHV} only. The pure plastic and pure biomass gasification cases were therefore scaled to that size for better comparability. The mixed plastic and biomass gasification case, where the whole downstream upgrading processes were investigated, however, was scaled to 524 MW_{HHV} to be comparable to the process concepts within the Skogskemi project.

In addition, as a considerable fraction of PVC is present in the total amount of plastics for chemical recycling it was decided to treat the fraction of construction waste – containing the majority of PVC – in a separate pre-processing unit in order to avoid too high concentrations of hydrogen chloride in the product gas. A low temperature pyrolysis for HCl removal (see Section 3.2.2) was assumed for the construction waste, with the remaining organic material being sent to the gasification unit. The scale of the process and the feedstock properties make fluidised bed gasification a suitable technology for this process. Indirect gasification was chosen within this project, partly due to the fact that data for model validation was available, and partly due to the experience on indirect gasification built up in Västra Götaland with the GoBiGas project¹ and Chalmers indirect gasification unit².

The modelling of mass and energy balances for the indirect gasification step are mainly based on data from two articles investigating biomass and plastics gasification as well as mixtures of the two fractions (Wilk & Hofbauer 2013a, Wilk & Hofbauer 2013b). The two articles contain complete datasets on pilot scale gasification experiments, allowing to adjust a previously developed model (Brau & Morandin 2014) to the corresponding experimental dataset. This way the mass and energy balance for the gasification step in the three cases can be estimated. As stated already in the literature review, the change in gas composition in for example a mixture of biomass and plastics feedstock cannot be correlated linearly to e.g. the plastics fraction, but the underlying chemical reaction pathways are far more complicated and not yet well enough understood to be modelled properly. It was therefore considered most convenient to pick experimental data presented in Wilk & Hofbauer (2013a & b) that is based on a feedstock mixture close to the one considered in this project, in particular with respect to the plastic fractions contained in the feedstock.

A simplified representation of the gasification model structure is represented in Figure 9. In a first steps the feedstock (characterised by its ultimate analysis) is decomposed into

¹ GoBiGas, http://gobigas.goteborgeneri.se/English_version/Start (2016-02-18)

² Centre for Indirect Gasification of Biomass – CIGB, <https://www.chalmers.se/hosted/cigb-en> (2016-02-18)

elements to allow the formulation of standard reactions in the modelling environment (Aspen Plus). Then, tars, methane, ethylene and other trace components present (HCl , NH_3) are formed adjusting their yield to fit the final product gas composition of experimental data. In a third step, an equilibrium reactor with only the light gases (CO , H_2 , CO_2 , H_2O) and char participating in the reactions is yielding the final product gas composition. Two major parameters are adjusted in this step to fit to the experimental data:

- the amount of char remaining after gasification (char yield)
- the fraction of steam actively participating to the reactions

The remaining char is separated from the product gas and combusted with air in a separate reaction chamber. In the real reactor the char is transported to the combustion chamber with the circulating bed material, the combustion reactions heating up the material, that way supplying the heat to the gasification reactions. If necessary for closing the energy balance, part of the product gas is combusted as well.

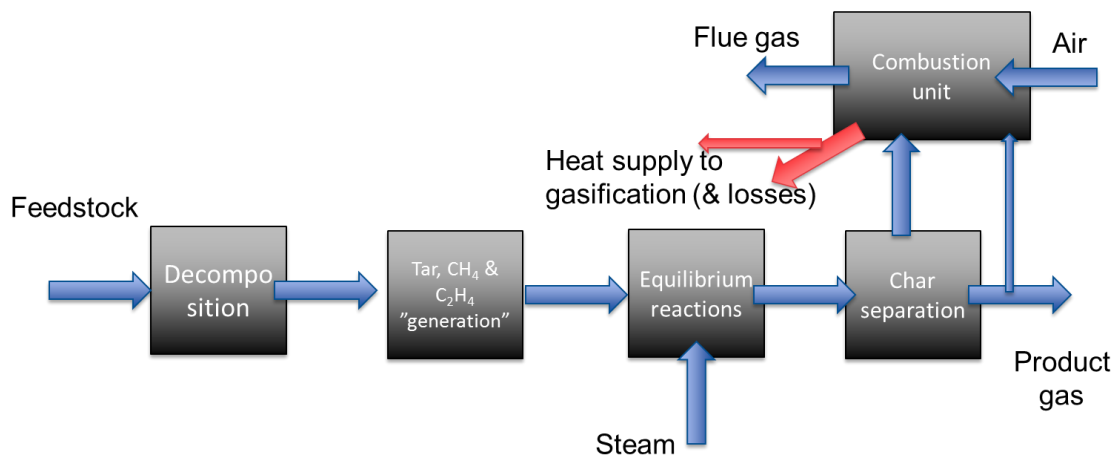


Figure 9: Basic illustration of the gasification model structure.

The feedstock characteristics for the different cases are illustrated in Table 17 with the mass-specific higher (and lower) heating value on a wet basis indicated as well.

Table 17: Proximate and ultimate analysis as well as heating values for the feedstock streams used in the three cases.

	Plastic waste to gasification (case 1 & 3) ^a	Construction waste plastics to HCl removal (case 1 & 3) ^a	Biomass (Forest residues) (case 2 & 3)
Proximate Analysis			
MC (wt-% wet)	0.075	0.145	40
FC (wt-% dry)	2.16	4.71	19.4
VM (wt-% dry)	97.22	94.85	77.7
Ash (wt-% dry)	0.60	0.42	2.9
Ultimate Analysis			
Ash (wt-% dry)	0.60	0.42	2.9
C (wt-% dry)	73.52	56.05	51.6
H (wt-% dry)	9.50	7.59	6.0
N (wt-% dry)	2.58	0.60	0.48
Cl (wt-% dry)	4,87	32.27	0.015
S (wt-% dry)	0.003	0	0.036
O (wt-% dry)	9,10	3.03	39.0
HHV (MJ/kg wet)^b	35.84	28.14	20.96
LHV (MJ/kg wet)^b	33.77	26.48	10.83

^a based on assumed plastic waste streams available for chemical recycling (see Section 2.3)

^b determined using correlation by Channiwalla & Parikh (2002) based on ultimate analysis

The two pure gasification cases – plastic and biomass – respectively were only modelled from feedstock to raw product gas in order to adapt and validate the model with literature data and to illustrate the basic differences in product gas yield and composition. The mixed biomass and plastic gasification case however was studied in more detail, the gasification island producing a clean gas ready for downstream synthesis processes.

4.4.2 Methanol synthesis, ethanol synthesis via methyl-acetate, and ethanol to ethylene

As a result of the simulation of gasification and gas cleaning section we observed that the syngas from plastics and biomass has an $H_2:CO$ ratio of about 2 which indicates that methanol can be synthesized without adjustment in a water-gas-shift reactor. In addition, this syngas is also suitable for ethanol and methanol synthesis via DME carbonylation and methyl-acetate hydrogenation.

Indeed, since the synthesis route to ethanol involves the production of DME we could have chosen to proceed directly to DME but we opted for an indirect DME synthesis via methanol and methanol dehydration as this still appears the most common technology. The modelling of the methanol synthesis section was based on previous work (Morandin and Harvey, 2014) while the modelling of the methanol dehydration, DME carbonylation, and methyl-acetate hydrogenation was mainly based on (Haro et al., 2012). The final step from ethanol to ethylene was not modelled but the results from (Arvidsson and Lundin, 2011) were used and scaled according to the ethanol mass flow rate.

The flow of syngas from the gas cleaning section was simply divided into two equal part, one proceeds to methanol synthesis and dehydration, the other is used for DME carbonylation.

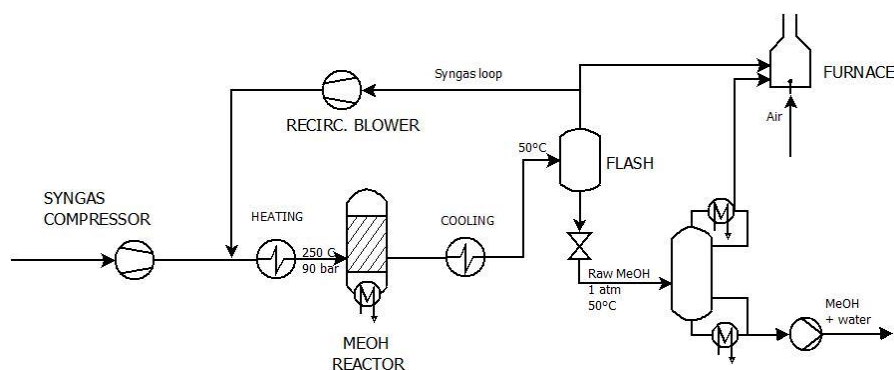


Figure 10: flowsheet of the syngas to methanol process

Figure 10a shows the flowsheet of the syngas to methanol process which was modelled in Aspen Plus and used to estimate the production of methanol which is subsequently sent to dehydration for DME production. A solid bed reactor layout was chosen for methanol synthesis, at a temperature of 250°C and at a pressure of 90 bar. Methanol synthesis was modelled considering the following reactions at equilibrium with 30°C temperature approach, where R1 is the methanol synthesis from CO, while R2 is the water gas shift and allows the synthesis of methanol from CO_2 :



The reactor products are cooled until 50°C and a flash tank is used to separate the gas from the raw methanol-rich liquid. About 4% of the gas is purged to avoid build-up of impurities and inerts and the remaining is recycled back to synthesis by means of compression to win the reactor pressure drops. The raw liquid methanol is expanded to atmospheric pressure

and sent to a stabilizer column where leftovers of methane, CO₂ and other impurities are removed.

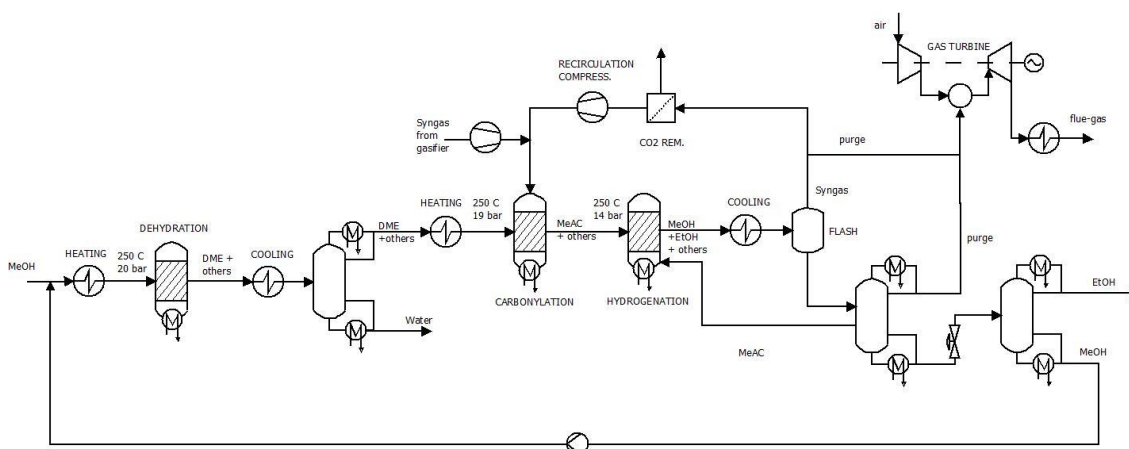


Figure 11: flowsheet of the methanol to ethanol process

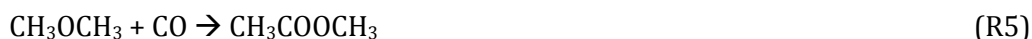
Figure 11 shows the flowsheet of the methanol to ethanol process which was modelled in Aspen plus and used to estimate the production of ethanol which is subsequently sent to dehydration for obtaining the final product ethylene.

Methanol with small amount of water is pumped, mixed with methanol recycled from the ethanol/methanol separation section, preheated, and sent to the dehydration step which occurs at 20 bar and at 320°C. This reactor was modelled considering the reactions at equilibrium with 20°C temperature approach, where R3 is the methanol dehydration into DME, while R4 is the dehydration of traces of ethanol:



The product from dehydration is cooled and sent to a distillation column, where water is recovered as bottom product and DME rich gas is obtained as top product. This stream is then preheated to 250°C and sent to the carbonylation reactor.

Carbonylation reactor was modelled considering the following reaction at 45% conversion, which imposes the conversion of DME into methyl-acetate:



This conversion value is accompanied by a large syngas loop around the reactor to allow a molar ratio of CO to DME of about 10.

Carbonylation is followed directly by hydrogenation according to the following reaction at 85% conversion, which imposes the conversion of methyl-acetate into methanol and ethanol:



The product is cooled and sent to a flash tank where methanol, ethanol and methyl-acetate are recovered as liquid and where syngas is obtained at the top. Part of this syngas is purged and sent to combustion but most of that is cleaned of CO_2 and recycled back by compression to the DME carbonylation reactor.

The methanol, ethanol and methyl-acetate stream is sent to a separation train where the methyl-acetate is recovered and sent back to hydrogenation. Methanol is sent back to dehydration and ethanol is recovered and sent to the final dehydration step.

Ethanol dehydration occurs in a multi-stage adiabatic reactor at 11 bar where ethanol and intermediate products are preheated up to 450°C . The reactor products are sent to a quench tower, a caustic tower and finally to a distillation column where ethanol is recovered and polymer grade ethylene is obtained.

4.4.3 Syngas for OXO synthesis via pyrolysis of automotive shredder light fraction and electronic waste

Figure 12 shows the proposed flowsheet for the production of syngas via pyrolysis of ASR and WEEE.

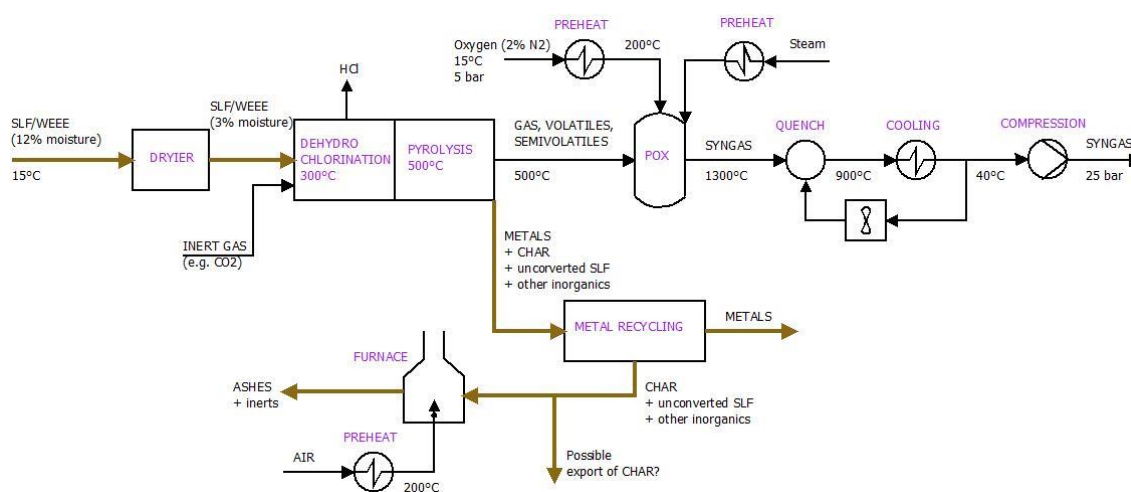


Figure 12: Flowsheet of the pyrolysis process for production of syngas from ASR and WEEE

The waste streams are first dried to remove moisture by direct contact with low temperature flue gases from the furnace. Similar to gasification of plastics rich in PVC, we assumed here that the waste stream is heated up to 300°C where PVC is decomposed and HCl is recovered.

The waste stream is further heated up to 500°C in the pyrolysis reactor. This temperature was chosen to prevent aluminium melting in order to allow for high recovery of this metal and also because this appears the temperature considered in the literature for similar technologies (Day et al., 1999).

The whole pyrolysis reactor should work in inert atmosphere to prevent oxidation. For this purpose it was assumed that a stream of inert gas is used. While most of the small scale applications use nitrogen, this is not possible when the whole pyrolysis gaseous product is used for syngas production. So in this work this stream may be considered a stream of CO₂ which is separated downstream and recycled back into the feeding system prior dehydrochlorination. It was not possible to estimate the flow of such stream and therefore it was neglected from the mass and energy balance since it does not affect the net product stream.

There are several possible alternatives to using CO₂ as discussed in Chapter 3.

- One option is to use nitrogen and then use a separation step to recover the heavier hydrocarbons in liquid phase which are then further sent to partial oxidation. The gaseous product rich in nitrogen can be partially recycled and the purge must be burnt. This layout requires a constant supply of nitrogen and part of the gaseous products are lost in combustion.
- A second option is to use steam. Steam may initiate secondary reactions especially if metals are present in the substrate. Water can be recovered by condensation.
- A third option is to recirculate the product gases or syngas. This implies that some hydrocarbons in the recirculated gas may be exposed to pyrolysis for a longer time and therefore secondary decomposition may occur.
- Finally, it is also possible to create a vacuum environment. This is particularly effective solution with batch autoclave type of reactor. A semi-continuous process could be realised by arranging several units in parallel.

The second and third options are promising and should be further explored. In this work it was not possible to pursue such concepts due to complete absence of data and methods to estimate secondary reactions in case of steam dilution or gas recirculation.

The pyrolysis of ASR and WEEE was modelled as yield reactor but the product distribution was modelled separately according to different literature data and assumptions as explained hereafter.

4.4.3.1 ASR Pyrolysis

The product distribution of the pyrolysis of ASR was modelled considering the data published in (Day et al., 1999) and adjusting the gas and solid yields to close the element balance of the organic fraction according to the ultimate analysis of ASR provided by Stena Metall. The ultimate analysis of ASR provided in (Day et al., 1999) and of ASR considered in this work is shown Table 18.

The following composition of the ASR considered in (Day et al., 1999) (%wt): moisture 2.6, organic 39.3, inert 58.1. The dry ASR results therefore composed of 40.3% of organic matter and 59.7 % of inert material.

One problem to be solved when deriving the composition of the organic material in ASR from the ultimate analysis is to understand how much oxygen is organic and how much is inert. By element balance, the organic oxygen in ASR considered in (Day et al., 1999) results 6.7 % of the total dry matter. The organic oxygen in Stena Metall ASR was considered in similar proportion to carbon as in (Day et al., 1999). We derived therefore a “revised” ultimate analysis of the Stena Metall ASR as shown in Table 18. The organic fraction of this “revised” ASR was then further used to estimate the product distribution using the data from (Day et al., 1999).

Table 18: proximate and ultimate analysis of ASR

	(Day et al., 1999)	Stena Metall ASR	"Revised" Stena Metall ASR
Proximate analysis (%wt)			
moisture	2.6	12	12
Organic (volatiles +fixed carbon)	39.3	n.a.	44.7
inert	58.1	n.a	43.4
Ultimate analysis (%wt)			
C	27.9	35.3	35.3
H	4	4.5	4.5
N	0.9	0.9	0.9
S	0.3	0.3	0.3
Cl	0.5	1.2	1.2
Others, of which	66.4	57.8	57.8
Metals, ashes, etc.	59.7	40	49.3
Oxygen	n.a.	17.8	9.3
Derived organic-O	6.7	n.a.	8.5
Derived ultimate analysis of organic matter (%wt)			
C	69.1		69.6
H	9.9		8.9
N	2.2		1.8
S	0.7		0.6
Cl	1.2		2.4
O	16.7		16.9

As shown in Table 18, the derived ultimate analysis of the organic matter for the "revised" ASR composition is not that different from that found for ASR considered in (Day et al., 1999) so it was assumed that the two substrates are quite similar and that the product should also be quite similar if the same pyrolysis reactor and operating conditions are used.

The following product distribution is shown in (Day et al., 1999): gas 8%, liquid 12%, solids 80%. The solids are composed of 8% char and 85% of inert plus ashes, which leaves an extra 7% of unreacted organic substrate. By calculating these solid fractions as fraction of the total feed and knowing that 58.1% of the feed is inert, we calculated that about 6.4% of the feed is converted into char, 10% of the feed is converted into ashes, and about 5.6% of the feed remain unconverted. These results in the following yields from the organic fraction: gas 19.1%, liquid 28.6%, char 15.3%, unconverted organic 13.4%, ashes 23.6%. These appear quite poor results, especially since unconverted organic and ashes amount together for about 40% of the organic fraction of the feed.

From this data the hydrocarbon distribution shown in Table 19 was derived based on the composition of gas and liquid yields reported (Day et al., 1999). Note that in this reference, the qualitative distribution of hydrocarbon from GS/MSD analysis is shown (% area), which was instead here assumed the actual composition of the gas and liquid (%wt). Such assumption introduces further uncertainty on our estimates.

These hydrocarbons are sent to partial oxidation while char, unconverted organic material, ashes and all the inert material (including metals) are removed and sent to metal recovery. After metal are removed, char and unconverted material are sent to combustion in a furnace.

Table 19: Assumed composition of the gaseous product from ASR pyrolysis as fraction of the organic matter in the feed.

	(wt. frac. of organic)	Note
H ₂	0,011859	gas fraction in (Day et al., 1999)
CO	0,011859	"
CH ₄	0,011859	"
CO ₂	0,123334	"
c ₂ h ₄	0,005930	"
c ₂ h ₆	0,005930	"
c ₃ h ₆	0,014231	"
c ₃ h ₈	0,005930	(sum of "gas": 19.1% of organic)
benzene	0,0167	liquid fraction in (Day et al., 1999)
toluene	0,0161	"
1-hexene	0,0160	"
pentane	0,0153	"
styrene	0,0130	"
2-butanone	0,0123	"
2,4 dimethyl-1-heptene	0,0111	"
1-propene, 2-methyl	0,0100	"
1-heptene	0,0083	"
ethylbenzene	0,0082	"
2,3-pentadiene	0,0079	"
2-methylfuran	0,0078	"
cyclopentene	0,0077	"
1-pentene	0,0075	"
1-octene	0,0070	"
3-pentanone	0,0060	"
n-decane	0,005778	assumed, C10
1-decene	0,005778	"
isobutylcyclohexane	0,005778	"
n-butylbenzene	0,005778	"
n-undecane	0,005778	assumed, C11
1-undecene	0,005778	"
1-methylnaphthalene	0,005778	"
n-pentylbenzene	0,005778	"
n-dodecane	0,005778	assumed, C12
1-dodecene	0,005778	"
1-ethylnaphthalene	0,005778	"
n-hexylbenzene	0,005778	"
n-tridecane	0,005778	assumed, C13
1-tridecene	0,005778	"
1-n-propylnaphthalene	0,005778	"
n-heptylbenzene	0,005778	"
n-tetradecane	0,005778	assumed, C14
1-tetradecene	0,005778	"
1-n-butylbenzene	0,005778	"
n-octylbenzene	0,005778	(sum of "liquid": 28.6% of organic)

4.4.3.2 WEEE Pyrolysis

The pyrolysis of WEEE was modelled in a similar way but data from two different references were used. The overall yield of gas and solids were estimated based on data reported in (de Marco et al., 2008) for electronic waste with similar ultimate analysis. The composition of the pyrolysis product was instead estimated based on the composition data reported in (Moltó et al., 2009). In this later study, electronic waste with a slightly different composition than the one considered in our project was used. In all the cases pyrolysis was conducted in inert atmosphere at 500°C which correspond to the same operating conditions considered in this work.

The compositions of the electronic waste reported in these references and provided by Stena Metall are shown in Table 20.

Table 20: proximate and ultimate analysis of WEEE.

	(de Marco et al., 2008) – mobile phones	Stena Metall WEEE	“Revised” Stena Metall WEEE	(Moltó et al., 2009)
Ultimate analysis (%wt)				
C	70.1	70.6	70.6	63
H	5.7	6.5	6.5	5.7
N	1.8	1.7	1.7	0
S	n.a.	0.04	0.04	1.7
Cl	n.a.	0.7	0.7	n.a.
Organic-O	6.8	n.a.	6.06	n.a.
Others (incl. inorganic O)	15.6	n.a.	14.4	n.a.
Others (w/o O)	n.a.	7.5	7.5	n.a.
Inorganic O	n.a.	n.a.	6.9	n.a.
Total O	n.a.	12.96	12.96	n.a.
Others + total O	n.a.	n.a.	20.46	29.6
Derived ultimate analysis of organic matter (%wt)				
C	83.6		82.48	?
H	6.75		7.59	?
N	2.13		1.99	?
S	n.a.		0.05	?
Cl	n.a.		0.82	?
O	8.06		7.08	?

In (de Marco et al., 2008) the following yields are reported (%wt): gas 12.3, liquid 57.4, solid 30.3. It is also stated that the solid fraction of the product has the following ultimate analysis: ashes 68.2, C 29.5, H 1.3, N 0.8.

By assuming that “ashes” includes the inorganic part of the input waste stream (14.4 % in case of “revised” WEEE), this means that an additional 6.3 % of the substrate, i.e. of organic

nature, leaves the pyrolysis in form of ashes. The carbon in the solid fraction is considered to leave in form of char, which yield therefore corresponds to about 9.5% of the feed.

Table 21: Assumed composition of the gaseous product from WEEE pyrolysis as fraction of the organic matter in the feed.

	(wt. frac. of organic)
styrene	0,2669465
CO ₂	0,0154498
phenol	0,1678095
bisphenol A	0,0726958
p-isopropenylphenol	0,0672411
alfa methyl styrene	0,0385424
phenol 4 methyl ethyl	0,0327346
benznebutanenitrile	0,0266366
benzene 1 ethenyl 4 ethyl	0,0186658
toluene	0,0180731
phenol p-tert-butyl	0,0161182
ethylbenzene	0,0091816
methane	0,0082483
p-ethylstyrene	0,0066339
xylene	0,0046475
methyl phenol	0,0045340
4 ethyl phenol	0,0039476
propyne	0,0034368
1,3 dyphenylpropane	0,0033233
2-aminoquinolene	0,0030647
2 methyl pehol	0,0025350
proylene	0,0021314
ethylene	0,0020495
ethane	0,0018351
benzene cyclopropyl	0,0016206
trans-2-butene	0,0015576
cyclohene 4 ethenyl	0,0014819
isobutene	0,0014441
benzene	0,0013053
benzene 1-methylethyl	0,0012738
adamantane 1,3 dimethyl	0,0012738
ethanone 1 (2-hydroxi phenyl)	0,0010720
benzene propyl	0,0009964
para-alfa-cumilfenol	0,0009522
propane	0,0009333
benzil nitrile	0,0008891
benzene acetaldehyde alpha methyl	0,0008450
p-xylene	0,0007946
benzene 3 butenyl	0,0006747
benzonitrile	0,0006558

The products that are not recovered as solids are categorised into gas and liquids in (de Marco et al., 2008) but no composition is available for these fractions. To produce an estimate of the hydrocarbon distribution it was therefore necessary to consult another reference. In (Moltó et al., 2009), the results of analysis of products from pyrolysis of electronic waste are presented. These data were used to estimate the hydrocarbon distribution in the pyrolysis gaseous products shown in Table 21. Note that the value of the yield of CO₂ was considerably reduced in order to satisfy the element balance.

It is possible to see that large amount of styrene, bisphenol-A, phenol and CO₂ are produced which are indicative of decomposition of polymers such as PC, ABS, and PS. Methane, and toluene and polycyclic aromatic compounds are also abundant.

4.4.3.3 Syngas production

The product gas at 500°C is sent to a partial oxidation step where in presence of oxygen and steam is reformed mainly into a mixture of H₂, CO, CO₂, water and with some traces of other hydrocarbons.

This partial oxidation step is modelled as a Gibbs reactor and the flow of oxygen is adjusted to obtain a temperature at the outlet of about 1300°C. The steam injection is adjusted to prevent carbon deposition.

The syngas obtained is too hot for heat exchanging and therefore is mixed with some syngas recycled from a downstream process point to reach a temperature of 900°C after which is cooled by heat exchanging, compressed to 25 bar and sent to OXO synthesis. In fact, the H₂:CO ratio in the resulting syngas was found of about 0.9 which was considered feasible for direct mixing with the syngas from natural gas partial oxidation at the site, as the syngas from ASR and WEEE pyrolysis is about one fourth of the total syngas needed for OXO synthesis.

4.5 Energy targeting

Thermochemical conversion processes are by definition processes where heat is produced and consumed at various temperature levels according to the various reactions required to convert the input waste streams into the desired products. Inevitably, part of the chemical energy of the raw material is converted into heat, such as via combustion. Rational heat management is therefore a key to high efficiency.

Due to the conceptual character of the study we aimed at estimating the maximum product yield and therefore ideal heat recovery was pursued. We adopted for this purpose an energy targeting method based on Pinch Analysis. This starts by establishing process flowsheets where cooling and heating steps are modelled as coolers and heaters. As a result of flowsheet simulation, all the heat loads and temperatures of thermal streams are obtained and the maximum heat recovery can be estimated through an algebraic procedure as explained in (Kemp, 2007) by imposing a minimum temperature difference between hot and cold streams. In this work a global minimum temperature difference of 10°C was assumed.

In practice, for our processes, the amount of heat available by gas cooling and from combustion of undesired by-products is significantly larger than the sum of all heating demands, as shown later in the result section. This means that heat management does not represent a significant limit to reaching the maximum conversion of input waste streams into desired chemical intermediates. Still, this excess heat can be recovered in form of steam which can be exported to the existing chemical plants to reduce the production of steam in

natural gas boilers. Since steam export is nevertheless a secondary objective compared to maximum product yield, such analysis can be performed after the excess heat from the thermochemical processes and its temperature profile is known, namely when the heat cascade or the grand composite curve (GCC) of such processes have been determined.

The maximum steam production was therefore established by solving a linear programming problem where the heat transfer feasibility is imposed as set of linear inequality constraints as explained in (Maréchal and Kalitventzeff, 1998). In this problem, the linear variables are the steam flows at the different levels with their upper bounds according to Table 16. The temperature profiles of steam productions were specified by imposing the target pressure and temperatures and considering a common feedwater temperature of 90°C.

This calculation was performed for the two formulated process concepts separately and by maximizing the production of steam at higher pressure levels from the excess heat of the gasification process first. Note that it is also necessary to take into account the reduction of high pressure steam generation from the natural gas partial oxidation plant for production of an equivalent amount of OXO-syngas obtained by ASR and WEEE pyrolysis. According to (Arvidsson et al., 2014), the specific production of HP steam is 1.2 tonne per tonne OXO-syngas. It was found that this can be satisfied by recovering the excess heat from the pyrolysis process only.

4.6 Accessing efficiency of thermochemical conversion

The objective of this work is to estimate the impact of the suggested processes on the global GHG emissions, which is the primary indicator that we retain for discussion of results.

On the other hand, this indicator does not give a clear picture of how efficient the conversion from the input waste streams to the desired products is performed and whether our modelling is sound compared to the literature. We use two indicators throughout the result section to keep track of such information:

Energy Conversion η , the ratio between the chemical energy rate of an outlet product stream and the chemical energy rate of the input waste stream, on HHV basis, as shown in (1).

For this purpose the mass flow rates \dot{m}_o and \dot{m}_i , respectively of the outlet product stream of the and the inlet waste streams are used.

$$\eta = \frac{\dot{m}_o \cdot HHV_o}{\dot{m}_i \cdot HHV_i} \quad (1)$$

Carbon Conversion χ , the ratio between the carbon in the main outlet product stream and the carbon in the inlet waste stream, as shown in (2). In addition to the mass flow rates of inlet and outlet streams, the mass fractions x_C of carbon in these streams are used.

$$\chi = \frac{\dot{m}_o \cdot xC_o}{\dot{m}_i \cdot xC_i} \quad (2)$$

Note that this indicators can be used to keep track of the conversion along different points of the process chain, the difference being only the value of mass flow rate of the outlet streams and their characteristics (HHV and x_C) at different specified process boundaries. This allows for instance to compare η at the exit of the gasifier, which is equivalent by definition to the cold gas efficiency, with other values reported in the literature for similar gasifiers.

4.7 Estimation of GHG emission reduction potentials

The production of chemical intermediates from the identified waste streams has a direct impact on the GHG emissions at the Stenungsund chemical complex site, for instance by substitution of part of the natural gas used for syngas production or gas that is used in natural gas boilers. On the other hand, the production of ethylene from plastic waste streams and the reduction of the import of fossil ethylene do not create any significant change of site emissions but reduces the emissions somewhere else, primarily at the site where the imported fossil ethylene is produced.

To rigorously take account such global effects, it is necessary to extend the boundaries of the system to include all the flows of commodities and industrial activities that are somewhat affected by the changes connected to the implementation of waste-to-chemical processes, according to a life-cycle perspective. We introduce for this purpose Figure 13 and Figure 14. Although at the end a cumulative value of change in global GHG emissions is estimated, it is convenient to describe the various contributions associated with the two process concepts separately, that is for the process from mixed plastic waste and forest residues to ethylene (Figure 13) and for the process from ASR and WEEE to syngas with integrated metal recycling (Figure 14).

In these figures, the reference industrial activities or energy conversion technologies are shown in yellow boxes, the proposed waste-to-chemical plants are shown with green boxes, the commodities that are produced and consumed and that are assumed to be constant are shown with white circles, the fossil resource with blue circles, and biomass (forest residues or wood chips) with a green circle.

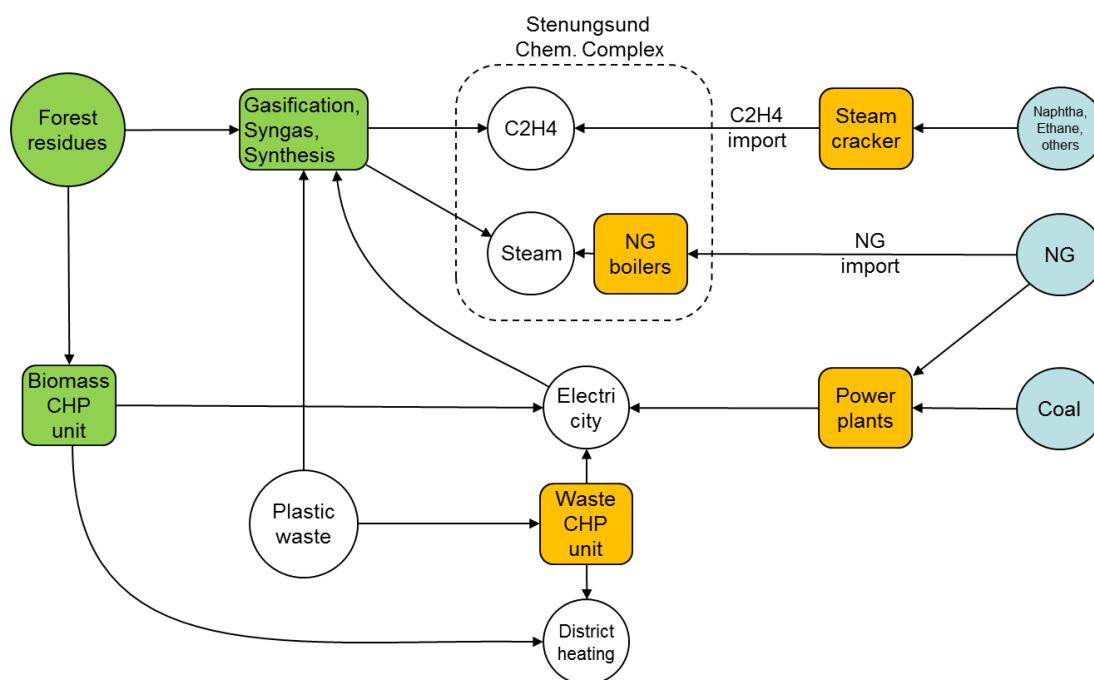


Figure 13. Overview of extended system that is used to estimate the GHG emission consequences of producing ethylene (C_2H_4) from mixed plastic waste and forest residues.

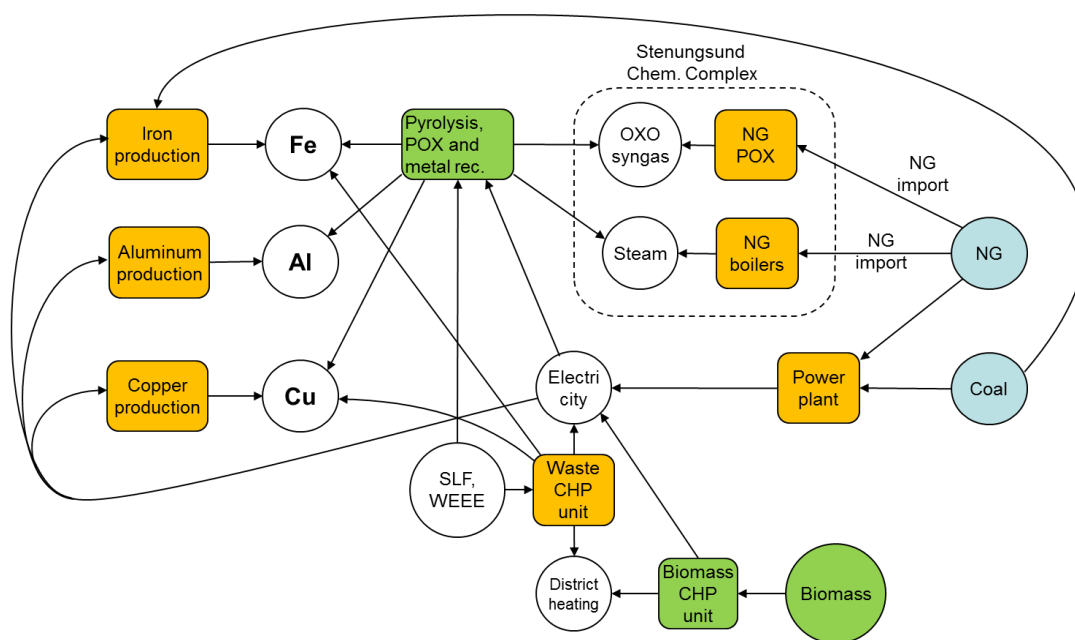


Figure 14. Overview of extended system that is used to estimate the GHG emission consequences of producing OXO-syngas from ASR and WEEE.

It should be observed that in these figures only the parts of the extended systems that are affected by significant changes are shown and some of technologies involved in production and utilization of the commodities that remain unaffected by the implementation of the proposed processes are left out. Note, in particular, that plastic waste and, to some extent, ASR and WEEE partly consist of polyethylene. When waste polyethylene is recycled into production of ethylene that ends up in polyethylene again, a loop of carbon is created and such stream of carbon does not leave the system in form of CO₂ anymore. This cycle has been neglected in our calculations since polyethylene is only a small part of the processed waste stream, and since the actual carbon conversion is lower than 1.

Table 22. Summary of assumptions of GHG emission factors and efficiencies of relevant processes

	Unit	HIGH scenario	LOW scenario
Iron production	t CO ₂ / t Fe	2.1	1.4
Aluminium production	t CO ₂ / t Al	22.5	13.0
Copper production	t CO ₂ / t Cu	3.3	1.9
Ethylene production (cradle-to-gate)	t CO ₂ / t C ₂ H ₄	1.44	1.15
OXO-syngas production via NG POX at Stenungsund site	t CO ₂ / t syngas	0.42	0.42
NG production (cradle-to-gate)	kg CO ₂ / MWh NG	42	42
NG combustion	kg CO ₂ / MWh NG	206	206
NG boiler efficiency at the Stenungsund site (LHV basis)	-	80%	85%
Marginal electricity production Reference technology (built-in)		Coal Cond.	NGCC
Electrical efficiency (LHV basis)	-	45%	64%
Emission factor	kg CO ₂ / MWh el.	913	388
Waste-to-energy CHP units electrical efficiency (HHV basis)	-	10%	30%
total efficiency (HHV basis)	-	90%	90%
Biomass CHP units electrical efficiency (HHV basis)	-	30%	30%
total efficiency (HHV basis)	-	90%	90%

Similarly, we have neglected the GHG emissions associated with the transportation of all the various commodities to the Stenungsund site.

Table 22 provides an overview of assumptions made for estimating the various contributions to the change in global GHG emissions, which are further described in the following sections. To take into account possible differences in performances of various industrial activities and energy conversion technologies, two scenarios were formulated: scenario “HIGH” where high emissions factors are considered, and scenario “LOW” where low emission factors are considered.

4.7.1 Gasification of mixed plastics for production of ethylene

As discussed in the introduction and shown in Figure 13, the assumption is that thermochemical recycling is alternative to energy recovery. This means that the carbon in

the mixed plastics is not released anymore into the atmosphere by combustion in combined heat and power (CHP) units but, depending on the overall carbon conversion, a large part of that ends up in ethylene.

We assume that the end-uses of the ethylene produced at the Stenungsund site, independently of whether it is produced via steam cracking or from waste, remain unchanged, thus no change in emissions were accounted for in the downstream value chain.

Accordingly, the GHG reduction contribution of producing ethylene instead of burning mixed plastics was calculated considering that the molar flow of avoided carbon dioxide is equal to the molar flow of carbon from plastics that ends up in ethylene.

4.7.2 Gasification of forest residues

Forest residues are the residual fraction of biomass that remains in the field after the main valuable part of the tree has been harvested. The carbon in forest residues comes from carbon dioxide sequestration during the tree growth. When forest residues are utilised for production of ethylene, part of the carbon ends up in ethylene, the remaining being lost in form of carbon dioxide along the process.

Similarly to mixed plastics, the net contribution to GHG emission reduction is calculated considering that the molar flow of sequestered carbon dioxide is equal to the molar flow of carbon from biomass that ends up in ethylene.

4.7.3 Pyrolysis of ASR and WEEE

The fraction of total ASR and WEEE produced in Sweden that was considered in this work, is the part that currently is sent to energy recovery. ASR and WEEE are used for production of syngas for OXO-synthesis.

Following the same assumptions for plastic waste, the GHG reduction contribution of producing syngas instead of burning ASR and WEEE was calculated considering that the molar flow of avoided carbon dioxide is equal to the molar flow of carbon from ASR and WEEE that ends up in syngas.

4.7.4 Metal recycling

Large quantities of iron (Fe), aluminium (Al), and copper (Cu) are present in ASR. WEEE is generally also rich in metals but in Sweden they end up mostly in the fraction that is sent to landfill and therefore are not relevant in this work.

The following amount of metals in ASR are entering the pyrolysis process: 7 440 tonne per year of iron, 2 000 tonnes per year of aluminium, 1 720 tonnes per year of copper.

Some of the iron and copper are today recycled from the ashes of ASR combustion in incineration plants but it was not possible to retrieve more exact information. We therefore assumed that the degree of iron and copper recycling from ASR are today respectively 30% and 10%.

For the proposed pyrolysis process with integrated metal recycling, we assumed the following degree of metal recycling: iron 70%, aluminium 70%, copper 90%. Although no specific technology or process concept was assessed, these values are indicative of feasible metal recycling targets.

As a result, the following incremental amounts of recycled metals were calculated: 2 980 tonnes per year of iron, 1 400 tonnes per year of aluminium, 1 375 tonnes per year of copper.

To estimate the contribution of metal recycling to global GHG emission reduction, these quantity of metals were multiplied by the specific emission factors of metal production. The values suggested in (Norgate et al., 2007) were used to formulate the HIGH and LOW scenarios of emission factors of metal productions shown in Table 22.

In particular for iron, the specific energy consumption for iron production and preparation for steelmaking shown in (Norgate et al., 2007) was used (HIGH: 18 GJ per tonne steel; LOW: 12 GJ per tonne steel). Although this is a cumulative value for what in reality is a combination of different energy carriers (e.g. coal, electricity, oil, etc.), in absence of more detail data it was assumed that specific energy consumption is equivalent to consumption of coal with specific GHG emissions (combustion plus cradle-to-gate) of 411 t CO₂ per MWh coal.

For aluminium and copper the specific GHG emission values in (Norgate et al., 2007) were adopted for production of new metals. It was assumed that recycled aluminium reduces by 95% the emissions of production of new aluminium and that recycled copper reduces by 90% the emissions of production of new copper.

4.7.5 Reduction of import of fossil feedstock for chemicals production

The proposed waste-to-chemical plants contribute to the reduction of import of fossil feedstock at the Stenungsund site.

By reducing the import of ethylene, the GHG emissions of ethylene production in marginal steam cracker units are avoided. Due to large variety of steam cracker technologies and feedstock it was decided to use a general value of GHG emission factor reported in the literature for ethylene. For the HIGH scenario the value of 1.44 tonne CO₂ per tonne ethylene proposed by DECHEMA was used (I.E.A., 2013). For the LOW scenario the value of 1.15 tonne CO₂ per tonne ethylene proposed by Plastic Europe was used (Plastic Europe, 2012).

The production of syngas for OXO synthesis applications contributes to the reduction of natural gas currently feeding a partial oxidation plant (Arvidsson et al., 2014). Due to partial oxidation of natural gas, some of the carbon in the feedstock leave the plant in oxidised form. This flow of carbon dioxide is avoided when introducing the proposed pyrolysis plant.

From (Arvidsson et al., 2014) a specific natural gas consumption of 0.57 tonne natural gas per tonne syngas was obtained.

Natural gas was considered as mixture of 80% methane, 5% ethane, 5% propane, and 10% butane, resulting in a mass fraction of carbon of 78%. Syngas for OXO-synthesis application is composed of 50%vol. of H₂ and 50%vol. of CO, resulting in a mass fraction of carbon of 40%. This results in a flow of 0.42 tonne CO₂ per tonne syngas. In addition the natural gas well-to-gate emissions were also considered as shown in Table 22.

4.7.6 Reduction of natural gas import for steam production by excess heat recovery from waste-to-chemical plants

The export of steam produced by recovering the excess heat from the waste-to-chemical processes contributes to a reduction of natural gas combustion in steam boilers at the site. The steam export targets were calculated following the energy targeting methodology. The natural gas consumption was calculated by dividing the steam heat load by the boiler efficiency. The GHG emissions of natural gas combustion were then calculated by multiplying the natural gas consumption by the specific emissions of natural gas combustion (well-to-gate emissions included).

4.7.7 Effects on marginal heat and electricity production technologies

One of the major consequences of shifting from a recycling strategy mostly based on energy recovery to a scenario where plastics is recycled into new chemicals or materials is the reduction in heat and electricity generation in waste-to-energy plants. This is particularly true for Sweden, where large amount of plastic is even imported since the large district heating networks often rely on waste-to-energy plant as base load technology together with industrial excess heat.

The effects on marginal heat production technologies are therefore largely dependent on the regional energy systems, being district heating network rather geographically limited. The detail analysis of such consequences is beyond the scope of this work but the authors are aware that the change in future energy market scenarios could impact a lot the results shown here as discussed later in the result section.

In this work we assumed that the reference built-margin heating production technology in Sweden are biomass CHP units. To take into account possible revamping of existing waste-to-energy plants and possible technological advancements different assumptions were made for the electricity and thermal efficiency in the HIGH and LOW scenarios as shown in Table 22.

In fact existing waste-to-energy plants have usually considerably lower steam values and electrical efficiency than state-of-the art biomass CHP units due to boilers corrosion limits and to advanced pollutant abatement systems.

By assuming that biomass CHP units replace the heat production from waste-to-energy plants, more electricity could be produced by CHP units (this is the case for the HIGH scenario here). By imposing a global electricity generation balance, this surplus of electricity contribute in turn to decrease the production in marginal electricity production technologies.

Electricity required by the waste-to-energy processes also contribute to the overall electricity balance. Ultimately, the contribution to global GHG emission of the change in marginal electricity production was calculated by multiplying the change in electricity production by emission factors for built-margin power plants following the indications in (Axelsson et al., 2009).

For the HIGH scenario we have assumed coal-condensing power plants and for the LOW scenarios natural gas combined cycle. The emission factors are shown in Table 22.

5 Results

5.1 Mass and Energy balances of selected configurations

5.1.1 Gasification based process concept

5.1.1.1 *Plastics gasification*

The major material and energy streams for the plastic gasification concept are illustrated in Figure 15.

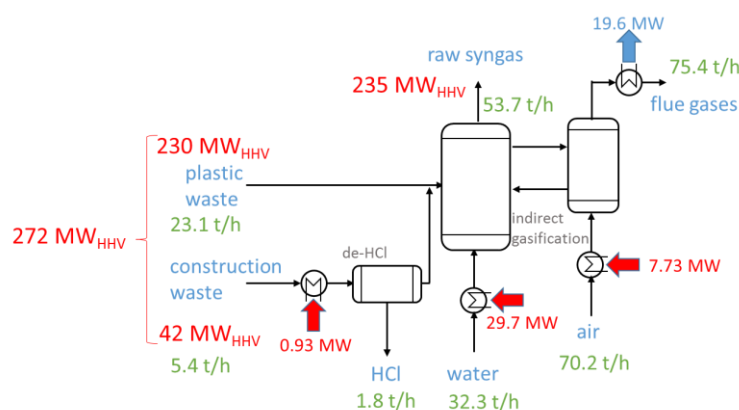


Figure 15: Pure plastic gasification flowsheet.

The pure plastic gasification results in an efficiency from feedstock to raw syngas of 86.4% on a HHV basis. This is considerably higher (nearly 10 % points) compared to the biomass gasification (76.9%, see Table 24) but the gas composition also differs substantially. As can be seen in Figure 16 and Table 23, a high fraction of methane and ethylene is present in the product gas, even implying high contents of tars. This increases the demand for downstream reforming in case a syngas only containing H_2 and CO is aimed at. At the same time plastic gasification is of interest if separation of light hydrocarbons from the product gas is an option. The results presented in Figure 15 are for the plastic stream identified within this project (see Table 17). The parameters for the model have been adjusted using experimental data on SLF, having a comparable composition to the plastic feedstock considered here. Figure 16 illustrates the experimental gas concentrations being used as reference, the concentrations obtained when adapting the gasification model to the experiments using the same feedstock, and finally the concentrations obtained using the tuned model with the plastic feedstock relevant for the present study. It also gives the distribution of the energy content in the product gas obtained, showing that a large part of the energy (67%) is contained in methane, ethylene and tars.

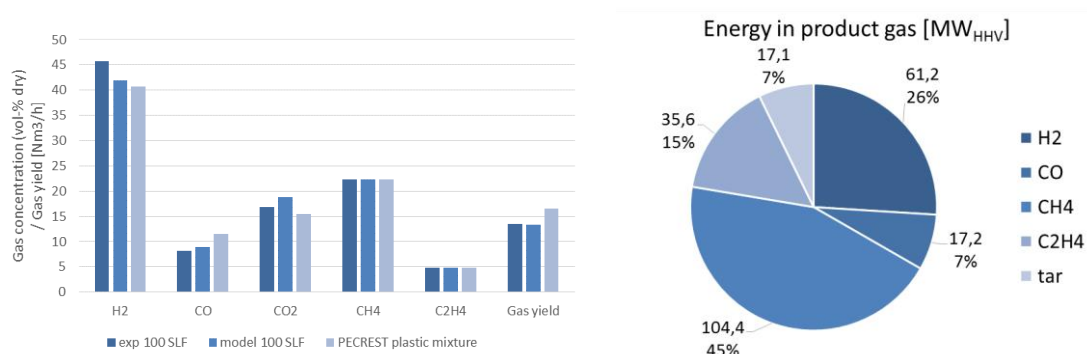


Figure 16: Comparison to Güssing plastic gasification experiments (Wilk & Hofbauer 2013a) (left) and composition of product gas for the plastic mixture in Table 17 (right).

As illustrated in Figure 15, the plastic stream containing high PVC fractions (construction waste) is treated separately for removal of a large fraction of the chlorine content. But still, as also illustrated in Table 23, the HCl concentration in the dry gas is about 1.7 vol-%, probably exceeding the acceptable level for potential downstream operations. Additional cleaning technologies need to be considered, alternatively cleaner plastic fractions are necessary for allowing for safe operation. The high tar content for pure plastic gasification is in accordance with published results.

Table 23: Gas concentration for the pure plastic gasification case with a thermal input corresponding to 272 MW_{HHV} using the plastic mixture specified in Table 17.

		Wet gas concentration	Dry gas concentration	
H ₂		25.6	40.8	vol-%
CO		7.3	11.6	vol-%
CO ₂		9.8	15.5	vol-%
CH ₄		14.0	22.3	vol-%
C ₂ H ₄		3.0	4.8	vol-%
Tars	Toluol	0.07	0.12	vol-%
	Naphtalene	0.11	0.18	vol-%
	Phenol	0.39	0.61	vol-%
HCl		1.1	1.7	vol-%
H ₂ S		6.21·10 ⁻⁴	9.88·10 ⁻⁴	vol-%
NH ₃		1.5	2.4	vol-%
H ₂ O		37.16	-	vol-%
total dry gas flow		42339		Nm ³ /h
tar concentration		40.77		g/Nm ³
efficiency (HHV)		86.4		%

5.1.1.2 Biomass gasification

The major material and energy streams for the biomass gasification concept are illustrated in Figure 17. As already mentioned above, the energy yield from feedstock to biomass is lower than for plastic gasification.

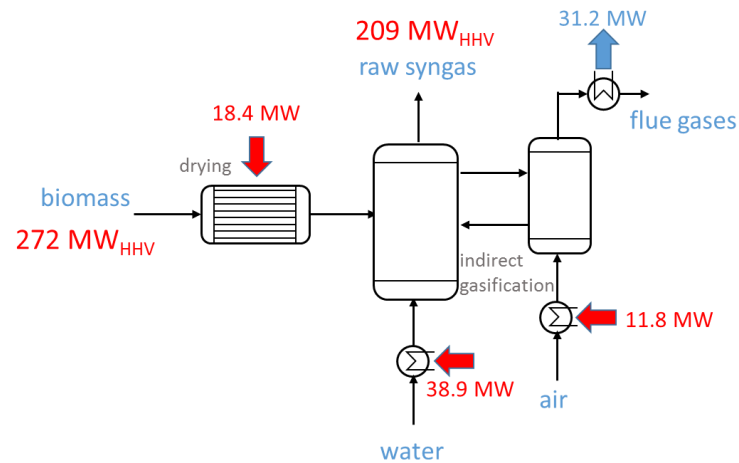


Figure 17: Pure biomass gasification flowsheet.

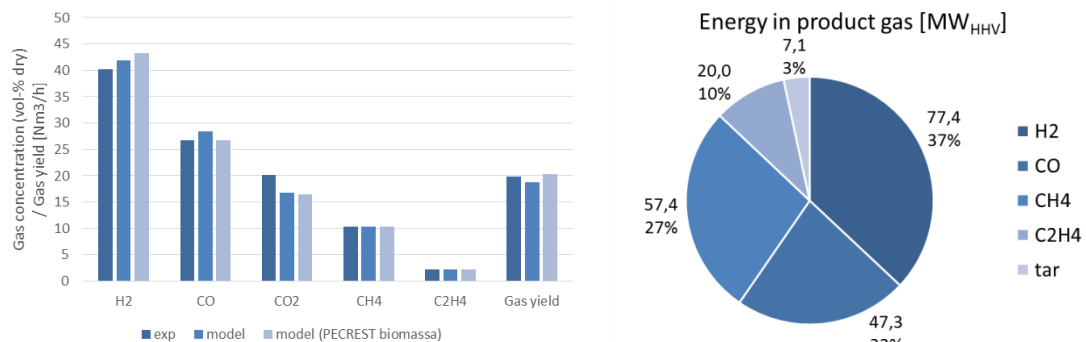


Figure 18: Comparison to Güssing biomass gasification experiments (Wilk & Hofbauer 2013a) (left) and composition of product gas for the forest residues (see Table 17) (right).

At the same time both methane and ethylene content, as well as tar levels are considerably lower. This is illustrated in Figure 18 and Table 24, presenting the experimental results used as reference, the modelling of the reference results as well as the results obtained from the tuned model applied on the biomass composition (forest residues) in the present study (Figure 18 left). The energy fraction of methane, ethylene and tars is lower than for plastic gasification, representing 40% of the product gas energy flow. In particular CO is present in a considerable higher fraction leading to a different H₂:CO ratio for the raw product gas. The lower hydrocarbon content also reduces the need for reforming in comparison to plastic gasification.

Table 24: Gas concentration for the pure biomass (forest residues) gasification case with a thermal input corresponding to 272 MW_{HHV}.

		Wet gas concentration	Dry gas concentration	
H₂		20.7	43.3	vol-%
CO		12.8	26.7	vol-%
CO₂		7.8	16.4	vol-%
CH₄		4.9	10.3	vol-%
C₂H₄		1.1	2.3	vol-%
Tars	Toluol	0.02	0.04	vol-%
	Naphtalene	0.03	0.06	vol-%
	Phenol	0.10	0.21	vol-%
HCl		4.04·10 ⁻³	8.46·10 ⁻³	vol-%
H₂S		0.01	0.02	vol-%
NH₃		0.33	0.69	vol-%
H₂O		52.2	-	vol-%
total dry gas flow		50505		Nm ³ /h
tar concentration		14.20		g/Nm ³
efficiency (HHV)		76.9		%

5.1.1.3 Combined plastic and biomass gasification

In Figure 19 the flowsheet for the combined plastic and biomass gasification is illustrated with the major energy flows and heat streams. This case is the one being the basis for the full scale evaluation including downstream synthesis of ethylene.

The gasification model has been adapted to fit for the feedstock mixture, using experimental data from gasification of an equal mixture of SLF and forest residues on an energy basis. The experimental and modelling (reference mixture and PECREST mixture) results are presented in Figure 20, even showing the energy distribution in the raw product gas from gasification.

The energy yield from feedstock to raw product gas is – as is to be expected – in between the value for pure biomass and plastic gasification, respectively. The tar content is lower than would be expected from a linear interpolation of the results from the pure feedstock, as has been demonstrated in previous work that also was the reference for model adaption here (Wilk & Hofbauer 2013a). After reforming in the autothermal reformer, the gas has an H₂:CO ratio of about 2.13 and the energy efficiency from feedstock to clean syngas is 76.3%. This is a rather optimistic value, mainly due to the assumption that all tars and higher hydrocarbons are converted to H₂ and CO without losses. This optimistic assumption will be cascaded downstream, resulting in an overestimation of final product yields that should be considered in the analysis of the results.

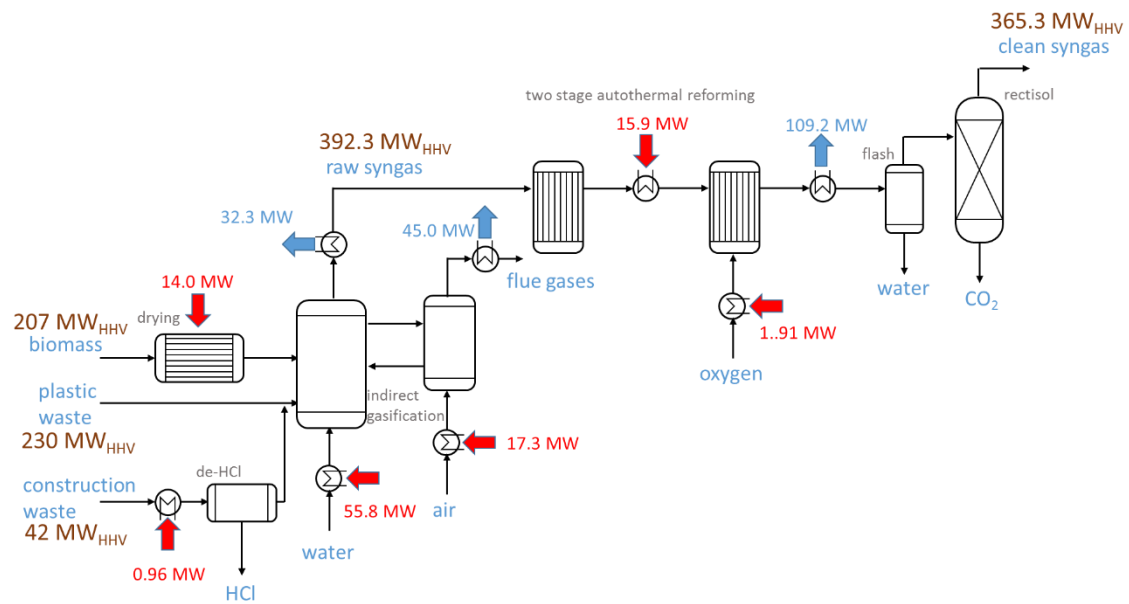


Figure 19: Gasification flowsheet for combined biomass and plastic feeding (being the basis for the full process chain evaluation).

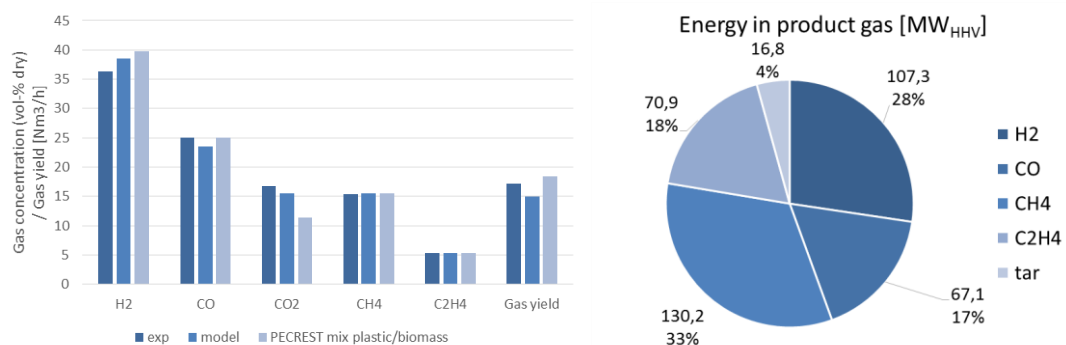


Figure 20: Comparison to Güssing SLF-biomass mixture (50/50 on energy basis) gasification experiments (Wilk & Hofbauer 2013a) (left) and composition of product gas for the mixture of the PECREST project (see Table 17) (right).

Table 25: Gas concentration for the gasification case using a mixture of plastic and forest residue with a total thermal input corresponding to 479 MW_{HHV}.

		Wet gas concentration	Dry gas concentration (raw syngas)	Dry gas concentration (clean syngas)	
H₂		21.2	39.7	65.4	vol-%
CO		13.4	25.1	30.7	vol-%
CO₂		6.1	11.4	3.0	vol-%
CH₄		8.3	15.5	-	vol-%
C₂H₄		2.8	5.3	-	vol-%
Tars	Toluol	0.03	0.06	-	vol-%
	Naphtalene	0.05	0.10	-	vol-%
	Phenol	0.18	0.34	-	vol-%
HCl		0.49	0.92	-	vol-%
H₂S		0.01	0.01	-	vol-%
NH₃		0.87	1.63	0.89 (N ₂) ¹⁾	vol-%
H₂O		46.5	-	-	vol-%
total dry gas flow		76315		107643	Nm ³ /h
tar concentration		22.32		-	g/Nm ³
efficiency (HHV)		81.9		76.3	%

¹⁾ N₂ from oxygen to ATR

5.1.1.4 Overall mass and energy balance around process for production of ethylene

The mass balances across the main process steps for production of ethylene from mixed plastics and forest residues are shown in Figure 21.

Overall, the yearly production of ethylene is estimated of about 124 kt which is about 60% of the current import of ethylene at the site and about 15% of the total ethylene used at the site. For this purpose all the ethanol produced by hydrogenation of methyl-acetate is dehydrated and all the methanol is recycled back to DME synthesis.

The total yearly flow of carbon entering the process with plastics waste and the forest residues is about 160 kt and 150 kt respectively, while the carbon leaving the process in form of ethylene is about 106 kt per year. This corresponds to a total carbon conversion χ of about 34%.

The values of the chemical energy rate of the main material flows are shown in Table 26.

Also, the methanol produced from the first syngas synthesis step (23.3 t/h) corresponds to a chemical energy rate of around 141 MW. Considering that this methanol is produced by synthesis of half of the dry-cleaned syngas, the energy conversion to methanol results of 59% (HHV basis) which is far greater than the values reported in literature for biomass based methanol production processes. We think this is associated with optimistic assumptions regarding the gasifier and reformer performances.

The overall energy conversion from waste to ethanol is 47% and is in line but somewhat greater than the value reported in (Haro et al., 2012) and maybe due to high methanol yield and optimistic assumptions on the hydro-carbonylation reaction especially the large syngas recirculation which may be very costly in practice. The overall conversion to ethylene is 46%.

Table 26. Summary of values of the chemical energy rate of the main material flows and energy conversion along the process for ethylene production.

Stream description	Mass flow rate (t/h)	HHV (MJ/kg)	Chem. energy rate (MW)	η
Forest residues	64	11.7	207	-
Total mixed plastics	28	34.4	272	-
Raw gas after gasifier	114.4	12.3	392	82%
Dry clean syngas after conditioning	55.3	23.8	365	76%
EtOH from MeAC	28.1	28.8	225	47%
Ethylene	15.5	50.9	219	46%

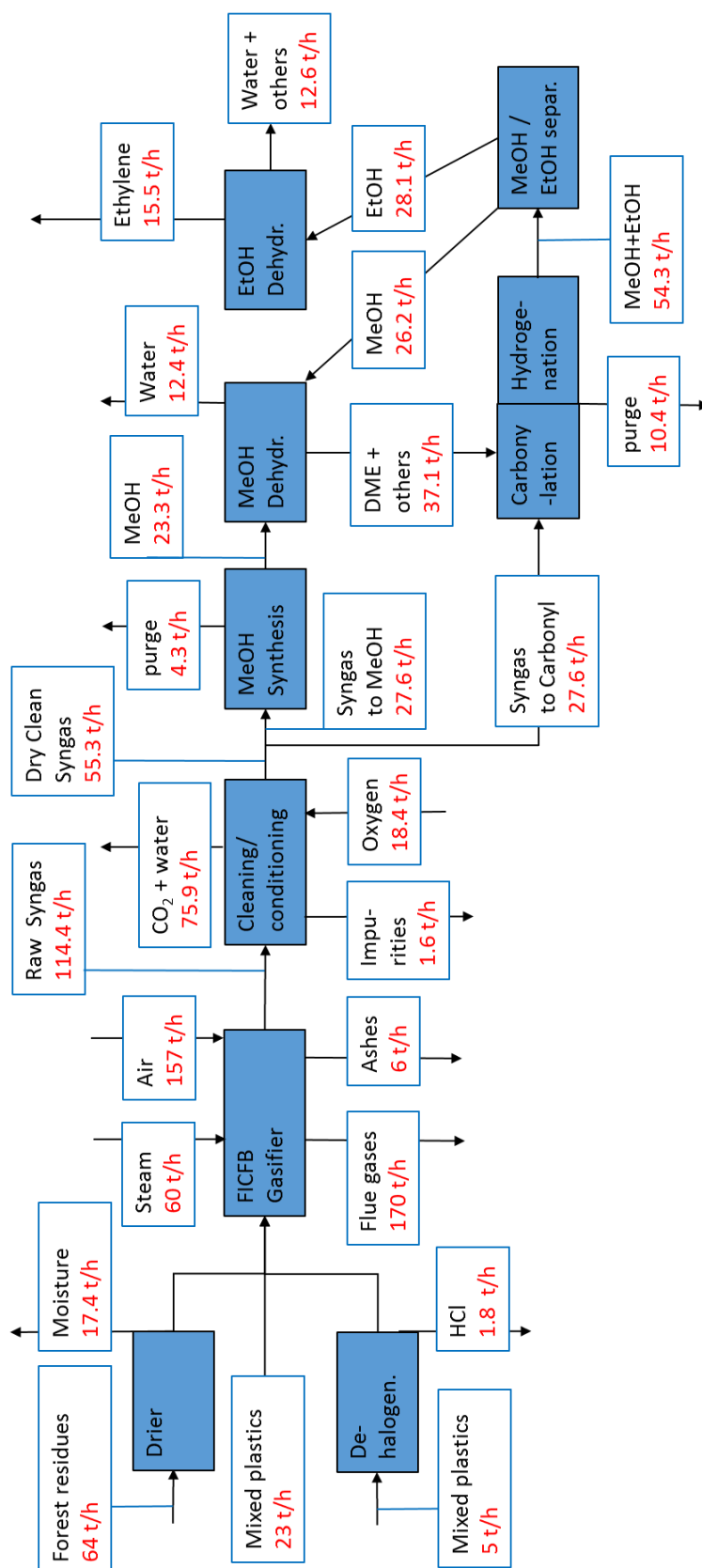


Figure 21. Mass balances around main process steps for production of ethylene from mixed plastics and forest residues.

5.1.1.5 Opportunities for steam export to the Stenungsund chemical plants

Large amount of excess heat is theoretically available from the waste-to-ethylene process as shown in Figure 22. This is also apparent from the value of energy conversion to ethylene which means that about 54% of the chemical energy rate in the input waste stream is ultimately released in form of heat as the no by-products are obtained. The theoretical amount of excess heat from the waste-to-ethylene process is about 200 MW as shown by the abscissa of the low-temperature end of the process grand composite curve. The difference between the input chemical energy rate (480 MW) and the ethylene plus excess heat (220+200) is about 60 MW which corresponds to all the heat losses at temperatures lower than the technically feasible heat recovery level.

In fact, not even all the 200 MW of excess heat but only 104 MW can be recovered for steam production, as shown with the dashed line in Figure 22.

The process also consumes electricity mainly for oxygen production in an air separation unit (about 4.8 MW) and for the various gas compressions (about 30 MW), e.g. before the methanol synthesis and for syngas loop around the methanol synthesis and the hydro-carbonylation reactors. The electricity demand for the waste-to-ethylene plant is therefore about 35 MW.

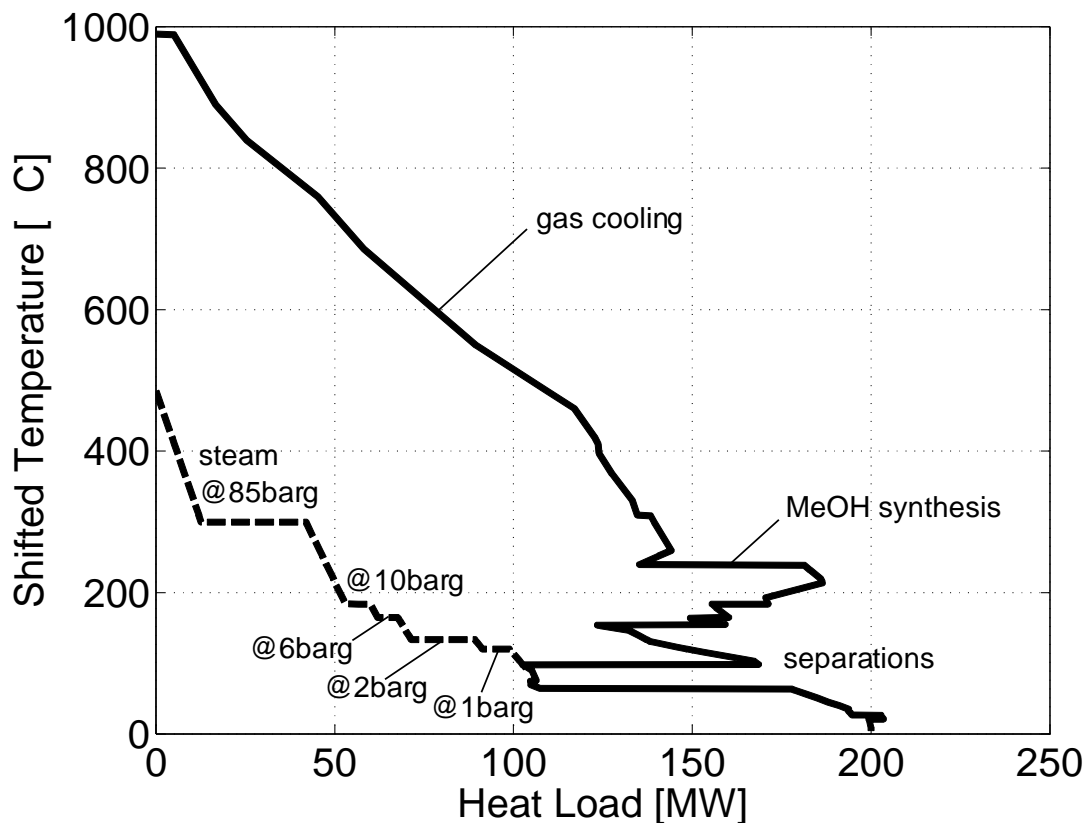


Figure 22. Grand composite curve of the process from waste to ethylene (solid line) and steam production targets at relevant pressure levels for the Stenungsund site (dashed line).

5.1.2 Pyrolysis based process concepts

5.1.2.1 Pyrolysis of Automotive shredder light fraction (SLF)

The main mass flow rates and the associated chemical energy rates as well as the heat loads associated with the operation of the main equipment units in the process based on ASR pyrolysis are shown in Figure 23 and Figure 24.

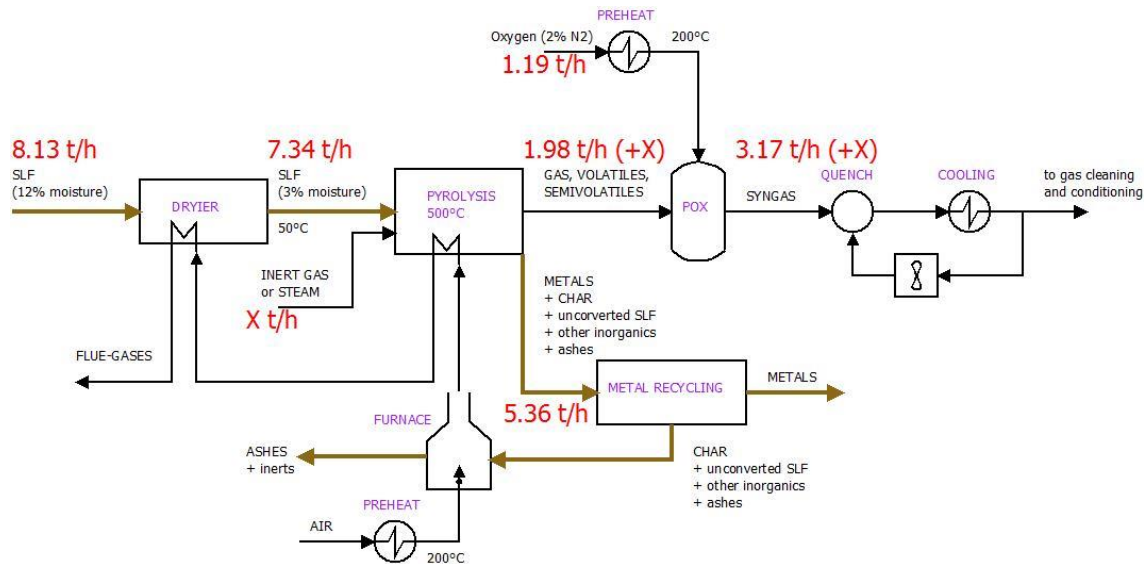


Figure 23: Mass flow rates of the main material flows in the process based on ASR pyrolysis

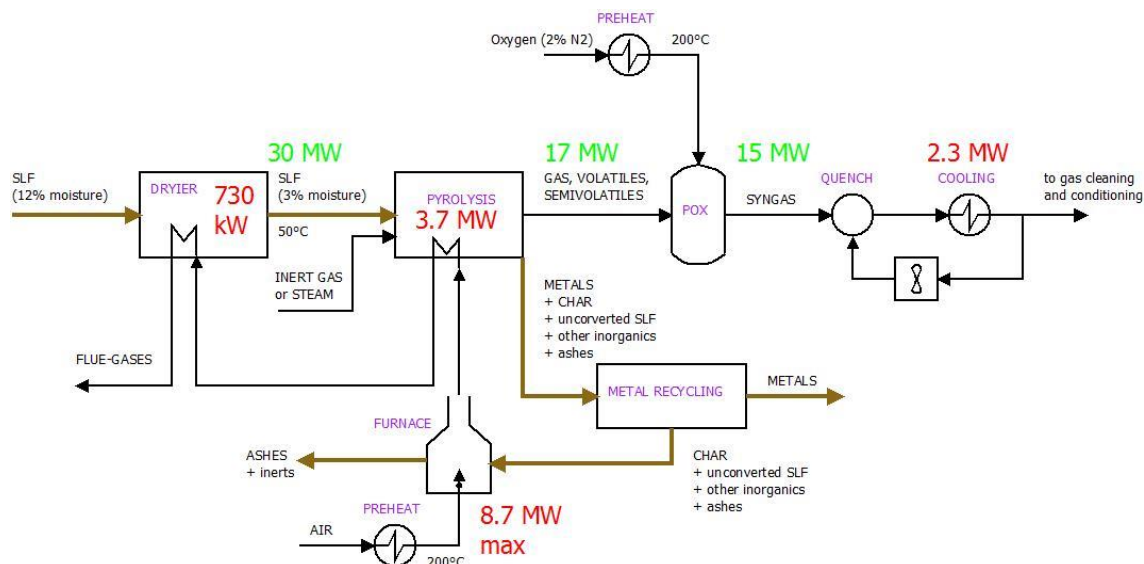
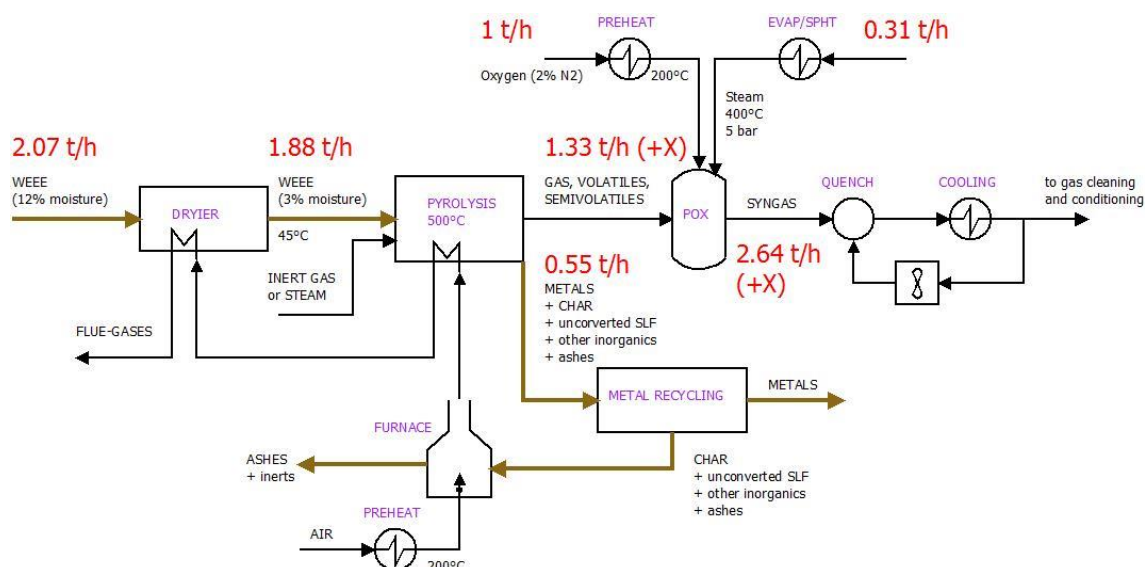


Figure 24: Chemical energy rates of main material flows and heat loads associated with operation of main equipment units in the process based on ASR pyrolysis.

The main mass flow rates and the associated chemical energy rates as well as the heat loads associated with the operation of the main equipment units in the process based on ASR pyrolysis are shown in Figure 25 and Figure 26.



The diagram illustrates the energy flows in a WEEE incineration plant. The process starts with WEEE (12% moisture) entering a DRYER (180 kW) where it is dried to 3% moisture. The dried WEEE (15.6 MW) then enters a PYROLYSIS unit (840 kW) at 45°C. The PYROLYSIS unit is heated by a FURNACE (1.6 MW max) which also receives AIR (200°C) and PREHEAT. The PYROLYSIS unit produces GAS, VOLATILES, SEMIVOLATILES (13.1 MW) which enter a POX (Partial Oxidation) unit. The POX unit is heated by a PREHEAT (200°C) and a 300 kW EVAP/SPHT unit. The POX unit produces SYNGAS (12.4 MW) which enters a QUENCH unit. The QUENCH unit is cooled by a COOLING unit (1.7 MW) which also receives METALS + CHAR + unconverted SLF + other inorganics + ashes from the PYROLYSIS unit. The COOLING unit then sends the gas to gas cleaning and conditioning. The PYROLYSIS unit also produces METALS (METAL RECYCLING) and METALS + CHAR + unconverted SLF + other inorganics + ashes (METAL RECYCLING). The METAL RECYCLING unit produces METALS and sends the remaining material to the FURNACE. The FURNACE also produces ASHES + inerts. The overall energy flows are: WEEE (12% moisture) 15.6 MW, DRYER 180 kW, PYROLYSIS 840 kW, POX 13.1 MW, QUENCH 12.4 MW, COOLING 1.7 MW, FURNACE 1.6 MW max, METAL RECYCLING 1.6 MW max, and 300 kW EVAP/SPHT.

Figure 26: Chemical energy rates of main material flows and heat loads associated with operation of main equipment units in the process based on WEEE pyrolysis.

5.1.2.3 Overall mass and energy balances around the syngas production process

The mass balances across the main process steps for production of syngas from ASR and WEEE are shown in Figure 27.

Overall, the yearly production of syngas is estimated of about 44 kt which is about 26% of the current amount of syngas used for OXO synthesis purposes at the Stenungsund site.

The total yearly flow of carbon in ASR and WEEE is about 30 kt per year, while the carbon leaving the process in form of syngas is about 17 kt per year. This corresponds to a total carbon conversion χ of about 57%.

Due to the high temperature partial oxidation step and gas quenching, the syngas stream leaving the process is almost completely clean of heavy hydrocarbons. The composition of the syngas obtained from the simultaneous pyrolysis of ASR and WEEE followed by syngas partial oxidation is (%vol.): H₂ 47, CO 51, CO₂ 1, N₂ 0.5, H₂S 0.2, H₂O 0.1. As anticipated above, the resulting H₂:CO ratio is close to the unity (0.93) and other compounds that should be removed prior OXO-synthesis are also quite low in concentration. This let us conclude that a dedicated syngas cleaning and upgrading section is not necessary. This syngas could be blended with the syngas produced from natural gas partial oxidation which composition can be adjusted to accommodate the small deviations of the H₂:CO ratio of the syngas from the pyrolysis process. In addition, a cleaning section already exists at the site which can be used to remove the impurities before OXO synthesis. Note however, that the syngas composition could change significantly in case of different proportion of ASR and WEEE in the feed.

The values of the chemical energy rate of the main material flows are shown in Table 27.

By performing separate simulation, we obtained that the energy conversion from ASR to syngas is about 51%, while the conversion from WEEE to syngas is about 79%. A straight linear composition of two processes results in an overall conversion from ASR and WEEE to syngas of 60%.

Both carbon and energy conversion of this process are larger than the corresponding values of the ethylene production process (χ 34%, η 46%). Such result should not surprise since ethylene production from syngas introduce further losses. On the other hand production of ethylene from fossil feedstock is also responsible for much larger carbon losses than syngas production from natural gas, so ultimately the impact on global GHG emissions may be similar.

Table 27. Summary of values of the chemical energy rate of the main material flows and energy conversion along the process for syngas production from ASR and WEEE.

Stream description	Mass flow rate (t/h)	HHV (MJ/kg)	Chem. energy rate (MW)	η
ASR	8.1	13.15	29.7	-
WEEE	2.1	27.09	15.6	-
Raw gas after pyrolysis	3.3	33.98	30.3	67%
Syngas after POX, cooling, to OXO	5.5	17.81	27.4	60%

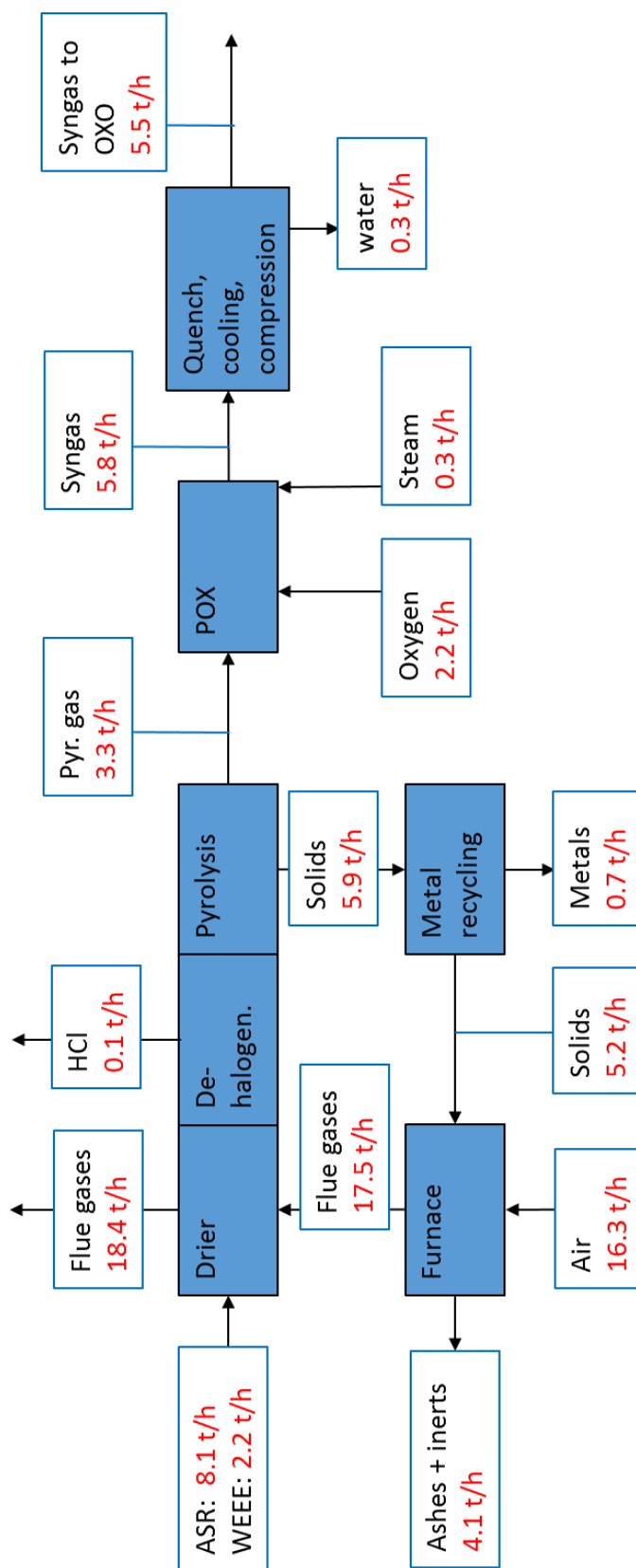


Figure 27. Mass balances around main process steps for syngas production from ASR and WEEE.

5.1.2.4 Opportunities for steam export to the Stenungsund chemical plants

Figure 28 shows the theoretical excess heat available from the syngas production process from ASR and WEEE and the steam production targets. The combustion of the solid residue, mainly char, and cooling of the combustion effluents and syngas from partial oxidation is sufficiently large to satisfy the pyrolysis heat demand. This leaves about 10 MW of excess heat which can almost entirely recovered in form of steam. The substitution of part of the natural gas derived syngas requires also to compensate for a proportional part of the 40 barg steam (around 4 MW) that is currently produced by recovering the heat from cooling the syngas from natural gas partial oxidation. Thus only about 6 MW of excess heat can be recovered in additional steam (here at 2 barg) that can contribute to a decrease in steam production at the site and result in natural gas savings.

The difference between the chemical energy rate in the input stream (45.3 MW) and the sum of chemical energy rate of the produced syngas (27.4 MW) and excess heat (10 MW) is about 8 MW which include all the heat losses that cannot be recovered for practical reasons plus the low temperature part of the heat in the combustion flue gases used for feedstock drying prior the pyrolysis section. The process also requires about 1.3 MW electricity for syngas compression prior OXO synthesis.

The production of oxygen for partial oxidation of the pyrolysis product also requires electricity consumption for an air separation unit but this is counterbalanced by the decrease in oxygen consumption for the natural gas partial oxidation and therefore does not contribute to any net increase in electricity use.

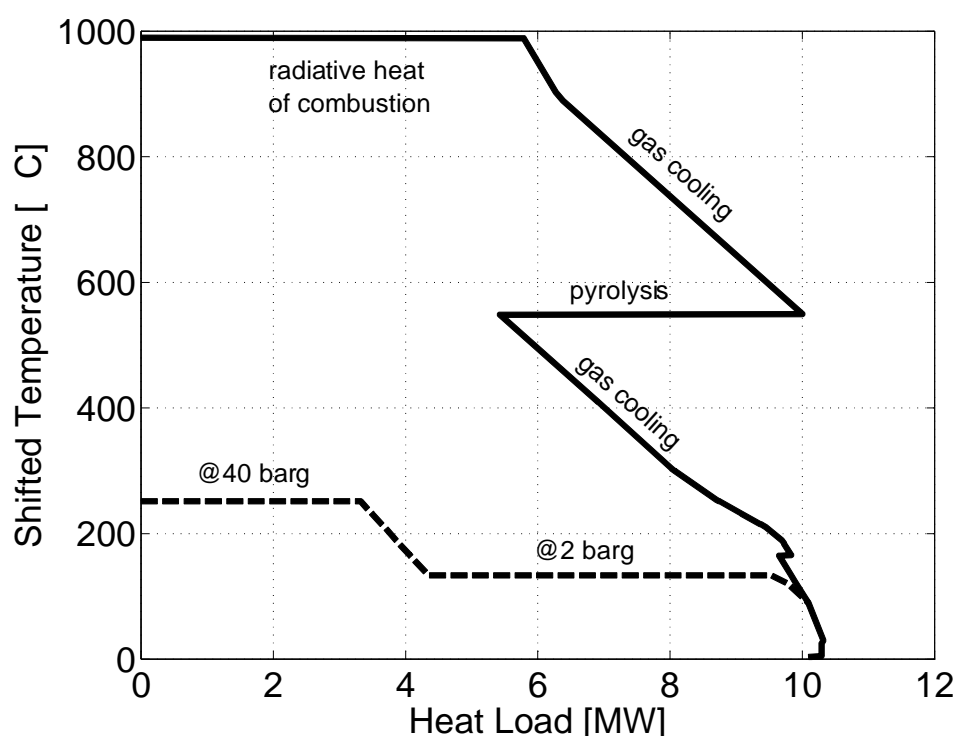


Figure 28. Grand composite curve of the process from ASR and WEEE to syngas (solid line) and steam production targets (dashed line).

5.1.3 Summary of mass and energy balances

Table 28 provides a summary of relevant input and output streams of the proposed waste-to-chemical processes. Among the products we have included also HCl which could be potentially integrated into PVC production at the site, although we do not have appropriate information to verify that the quality of the gas from dehydrochlorination step is sufficiently high to allow it.

Table 28. Summary of main input and output streams of the proposed waste-to-chemical processes

Stream description	Mass flow rate (t/h)	Amount per year (kt/y)	Percentage of site demand	Associated energy rate (MW)
Input				
Mixed plastics	28.4	228	-	271.7
Forest residues	63.7	510	-	207.0
ASR	8.1	65	-	29.7
WEEE	2.1	17	-	15.6
Electricity (incl. ASU)	-	-	-	36.4
Output				
Ethylene	15.5	124	~ 15%	219.4
Syngas to OXO	5.5	44	~ 26%	27.4
Steam @ 85 barg, 485°C	75.0	600	100%	62
Steam @ 40 barg	7	56	substitute POX	4
Steam @ 10 barg	12.4	99	69%	8.3
Steam @ 6 barg	9.8	78	100%	6.5
Steam @ 2 barg	38.2	251	100%	25
Steam @ 1 barg	12.3	98	100%	8
Iron	0.372	2.976	-	-
Copper	0.172	1.376	-	-
Aluminium	0.175	1.400	-	-
HCl	1.9	15.2	n.a.	-

5.2 GHG emission reduction potentials

5.2.1 Ethanol via thermochemical gasification of plastic waste and forest residues

The potential reduction of global GHG emissions of the process based on gasification of plastic waste and forest residues was estimated between 665 kt to 1060 kt of CO₂-eq per year based on the “low” and “high” scenario respectively. The various contributions are shown here in Figure 29 and Table 29.

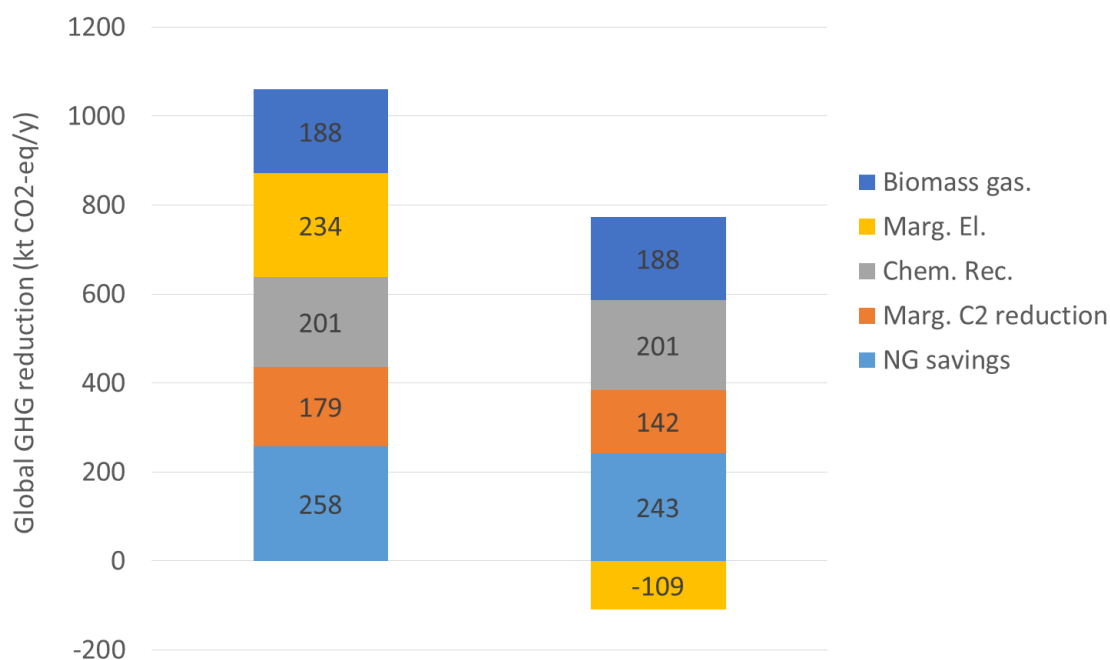


Figure 29: Estimated potential reduction of global GHG emissions of the waste-to-ethylene process

Table 29. Overview of contributions to the GHG emission reduction potential from the waste-to-ethylene process for the two scenarios formulated on the basis of different assumptions

Description of contribution	"High" scenario (kt CO ₂ -eq / y)	"Low" scenario (kt CO ₂ -eq / y)
plastics gasification to ethylene	266	266
Forest residues gasification to ethylene	188	188
Reduction of ethylene import	179	142
Reduction of NG combustion to boilers	258	243
Change in marginal electricity production of which...		
related to substitution of plastic energy recovery	490	0
related to import of electricity to process	- 257	- 109
Total estimated reduction of global GHG emissions	1060	665

5.2.2 Syngas for OXO-synthesis via pyrolysis of SLF and WEEE

The potential reduction of global GHG emissions of the process based on gasification of plastic waste and forest residues was estimated between 119 kt to 227 kt of CO₂-eq per year based on the “low” and “high” scenario respectively. The various contributions are shown here in Figure 30 and Table 30.

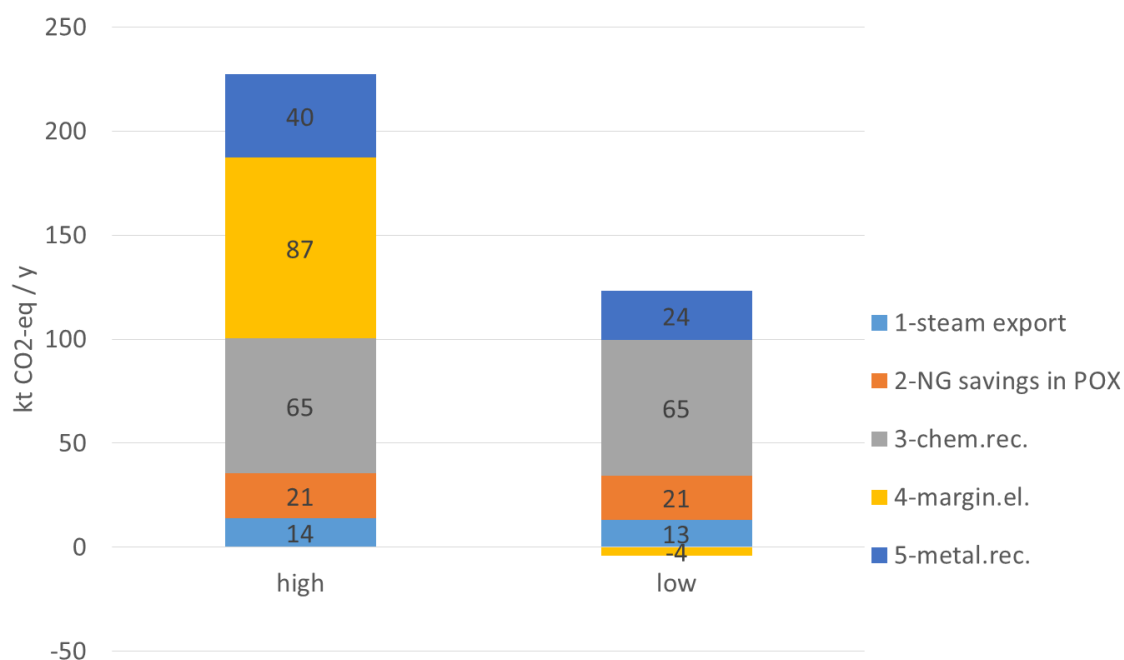


Figure 30: Estimated potential reduction of global GHG emissions of the ASR and WEEE pyrolysis to syngas process.

Table 30. Overview of contributions to the GHG emission reduction potential for the ASR and WEEE pyrolysis to syngas process for the two scenarios formulated on the basis of different assumptions

Description of contribution	“High” scenario (kt CO ₂ -eq / y)	“Low” scenario (kt CO ₂ -eq / y)
ASR + WEEE pyrolysis to syngas	65	65
Metal recycling	40	24
Reduction of NG partial oxidation	21	21
Reduction of NG combustion to boilers	14	13
Change in marginal electricity production related to substitution of ASR and WEEE en. rec.	97	0
related to import of electricity to process	-10	-4
Total estimated reduction of global GHG emissions	227	119

5.3 Summary of results

Figure 31 shows the estimated potential reduction of the global GHG emission by implementing the proposed waste-to-chemical processes and the various contributions according to the description in the methodology section. The values are reported in more detail in Table 31.

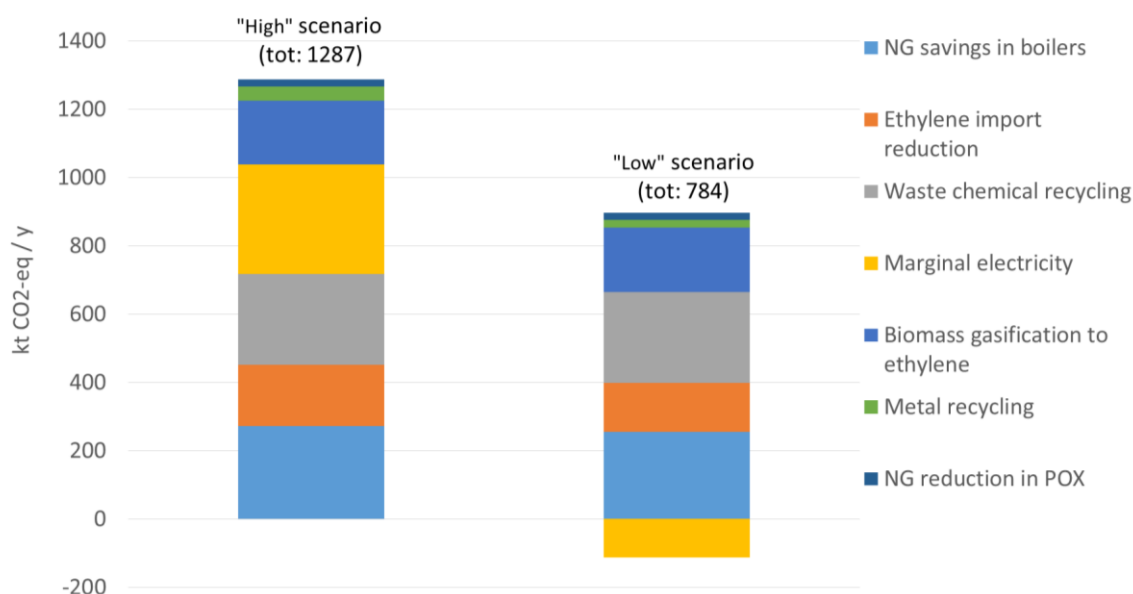


Figure 31: Potential reduction of GHG emission of the proposed waste-to-chemical processes for the two scenarios formulated on the basis of different assumptions

The “high” and “low” scenarios were formulated based on different assumptions on marginal technologies for the production of various commodities. This results in a large span of estimated GHG emission reduction potential which goes from about 1300 kt CO₂ equivalent per year in the “high” emission scenario to about 800 kt CO₂ equivalent per year in the “low” emission scenario. This is about the same order of magnitude of the current on-site GHG emissions of the Stenungsund chemical complex (about 900 kt CO₂-eq per year).

By looking at the different contributions, it is worth comparing the impact of plastics gasification with biomass gasification. If compared in specific energy terms, the gasification of plastics for production of ethylene contributes to about the same reduction of global GHG emissions as ethylene production via biomass gasification. Behind this result, lies an important assumption. Plastic waste is assumed constant and its chemical recycling is considered as alternative to combustion for energy recovery. Conversely, gasification of forest residue does not compete with an alternative utilization.

Table 31. Overview of contributions to the GHG emission reduction potential for the two scenarios formulated on the basis of different assumptions

Description of contribution	“High” scenario (kt CO ₂ -eq / y)	“Low” scenario (kt CO ₂ -eq / y)
Waste-to-chemical	266	266
of which ...		
plastics gasification to ethylene	(201)	(201)
ASR + WEEE pyrolysis to syngas	(65)	(65)
Forest residues gasification to ethylene	188	188
Metal recycling	40	24
Reduction of ethylene import	179	142
Reduction of NG partial oxidation	21	21
Reduction of NG combustion to boilers	272	256
of which ...		
due to steam export from ethylene process	(258)	(243)
due to steam export from syngas process	(14)	(13)
Change in marginal electricity production	321	- 113
of which...		
related to substitution of plastic energy recovery	(490)	(0)
related to substitution of ASR and WEEE en. rec.	(97)	(0)
related to import of electricity to process	(- 267)	(- 113)
Total estimated reduction of global GHG emissions		
of which..	1287	784
related to plastics and biomass to ethylene process	(1060)	(665)
related to ASR and WEEE to syngas process	(227)	(119)

Also, when comparing on energy basis, pyrolysis of ASR and WEEE contributes to a larger reduction of GHG emission (65 kt CO₂-eq per 45 MW) than gasification of plastics (201 kt CO₂-eq per 272 MW) which is due to larger losses in the process chain. This is somewhat compensated by two main other consequences: the emission reduction associated with avoided marginal ethylene production is much larger compared to the reduction in emission associated with syngas production via natural gas partial oxidation; much more steam can be produced by recovering excess heat from the waste-to-ethylene plant than from the pyrolysis plant, leading to higher reductions in GHG emission by avoided natural gas combustion in boilers. Another important aspect of distinction between the waste-to-ethylene plant and the pyrolysis plant is the large amount of electricity needed in the first case. This contributes to significant emissions in marginal electricity producer.

Overall, if compared on energy basis, pyrolysis of ASR and WEEE appears to contribute to larger emission reductions than the plastics and biomass to ethylene process. This is mainly due to the assumption of chemical recycling of plastics, ASR and WEEE replace energy recovery and that avoided production of electricity and heat in marginal CHP plants is compensated by biomass based CHP plants. In the “high” emission scenario we assume that this even contributes to higher electricity production for the same heating basis which reduces the production of electricity in coal condensing plants. Since in the ethylene process almost half of the input in energy basis is biomass, the process utilizing ASR and WEEE is favoured in this comparison since the impact in marginal heat and electricity production technology is proportionally higher. Also, the increase of metal recovery compared to current ASR and WEEE recycling technology has a minor but still positive impact which favoured this process when comparison is done in energy basis.

6 Conclusions

In the present work, process concepts for chemical recycling of waste streams for production of chemical intermediates at a Swedish chemical complex site were identified and their GHG emission reduction potentials quantified by keeping the energy recovery alternative as reference of comparison. The total Swedish waste stream of plastics, automotive shredder residues (ASR) and electronic waste (WEEE) currently sent to energy recovery were considered. Forest residues were also used as an input following a vision of feedstock flexibility and carbon-neutral production of chemicals.

The layout of the envisioned waste-to-chemical plant includes a process for production of ethylene via gasification of plastics and forest residues and a process for production of syngas for OXO-synthesis applications via pyrolysis of ASR and WEEE. Mass and energy balances were established by process flowsheet simulations and process integration opportunities were identified by applying an energy targeting methodology.

Based on rather optimistic assumptions it was found that about 120 kt of ethylene per year and about 44 kt of syngas can be produced which are respectively about 15% and 26% of the site demand of ethylene and syngas to OXO synthesis.

Considering that forest residues were also included among the input (about 40% in energy terms), these results are on one hand a sign that the contribution of chemical recycling to production of chemical and plastics may be moderate. On the other hand, among the input waste stream we have selected mixed plastic waste and very heterogeneous waste (ASR, WEEE) which may be very difficult to recycle using a material/mechanical strategy. Thus, these results are also quite encouraging and should motivate a further investigation of the economic feasibility of proposed concepts.

Overall, the estimated contribution to global GHG emission reduction lies in a range between 800 and 1300 kt CO₂-eq per year depending on the different scenarios of marginal technologies for production of ethylene, electricity and heat. This is about the same order of magnitude of the current on-site GHG emissions at the Stenungsund chemical complex site. This result is based on assumption that chemical recycling is alternative to energy recovery which in Sweden is done in CHP units connected to district heating networks. By diverting waste to chemical production, we assumed that biomass CHP units compensate for electricity and heat production and that this can even create a surplus of electricity in short term which in turns reduces the production of electricity in coal power plants. This results highlights that the climate consequences of the proposed recycling strategy are largely dependent, at least in Sweden, on the future development of the biomass prices and utilization. Note that another possible scenario is that more waste is imported to Sweden in the future. In such case, the consequences of chemical feedstock recovery from plastic waste, ASR or WEEE is largely dependent on the alternative end-of-life of plastic waste in the countries of origin and is therefore hard to estimate.

The results also show that an important reduction of GHG emissions can be obtained by recovering the large amounts of excess heat available from the thermochemical processes for production of steam which can be exported to the various chemical plants by appropriately placing the proposed processes close to or in the middle of the chemical complex site. This steam is about 70% of the steam currently produced at the site in natural gas boilers. The reduction of natural gas consumptions in steam boiler contributes to about 20 to 30% of the total GHG emission reduction potential which highlights the suitability of the Stenungsund site for large-scale implementation of biorefineries and waste-to-chemical plants.

6.1 Challenges and opportunities

The present project aimed at estimating potentials for feedstock recovery from plastic waste, ASR and WEEE. The actual implementation of the proposed concepts implies several challenges.

One of the most important issue for a successful implementation of feedstock recycling is getting rid of the impurities in the plastic waste (as well as ASR or WEEE) that may contaminate the downstream processes. The presence of large amount of PVC in the construction and demolition sector as well as in the waste streams from the other sectors implies that large quantities of Chlorine or even Bromine need to be removed prior high temperature thermal processes. This is a challenge that other processes proposed in the past have faced and that still represents a barrier to commercial applications.

We also realised that the scale of the proposed processes impose logistical challenges since it was assumed that only the plastic fractions in heterogeneous waste streams such as residual waste from the residential sector are processed. This may require advanced separation techniques or, alternatively, that the whole waste and not only the plastic is sent to feedstock recovery.

We see on the other hand that the scale of the process needs to be sufficiently large to justify heat recovery for steam production at the Stenungsund chemical site.

Thermochemical recycling of waste opens nevertheless a series of interesting opportunities.

The proposed processes can handle mixed waste streams that may be hard to recover in another way than energy recovery of landfill.

The processes are quite modular and different gasification or pyrolysis units could be built step-wise and possibly also be arranged in different ways. In this study gasification and pyrolysis were chosen at the basis of two separate process concepts and final products. However, one could think of using pyrolysis as a step prior to gasification.

Although the focus here was on plastic waste and forest residues were used only as a complement, biomass could be given the role of main feedstock while plastic waste or other waste could be used at a level such to improve the processing of biomass as highlight in the reference literature on co-gasification of biomass and plastics.

6.2 Recommendations

Based on the project findings we recommend the following:

- Investigate the economic feasibility of the presented concept with special attention to future development of prices of waste, biomass, metals, as well as to possible development of policy scenarios that may promote or hinder feedstock recovery from waste.
- Consider the possible application of chemical recycling to the processing of rest streams from plastic mechanical recycling.
- Investigate the technological alternatives for handling/separating PVC from mixed plastic waste.
- Expand the range of input streams to a waste refinery at the Stenungsund chemical complex site by including other waste such as municipal solid waste.
- Conduct more system studies where waste-to-chemicals is included as an alternative to waste-to-energy and investigate different development of the European energy market and waste disposal, including the scenario in which plastic waste or other heterogeneous waste streams are imported to Sweden for energy and feedstock recovery.
- Investigate the treatment of polyolefin rich mixed plastics in pyrolysis units for production of aliphatic oils to be sent to further upgrading in existing facilities at the Stenungsund chemical complex site.
- On a short term, focus on ASR and WEEE pyrolysis with integrated metal recovery. Nitrogen atmosphere could be used first and the gases and liquid sent to combustion. Afterwards, try to establish an upgrading strategy for the hydrocarbons.

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